

Deuterium isotope effects on the photoreduction of 9,10-phenanthrenequinone and benzophenone by 2-propanol

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Abstract

Reactive rate constants for the quenching of the triplet state of 9,10-phenanthrenequinone by 2-propanol were measured using laser flash photolysis and deuterium isotope effects for the abstraction of the alpha hydrogen (deuterium) were determined. The values of k_H/k_D were 1.69, 1.45, and 1.36 in carbon tetrachloride (CCl_4), chlorobenzene (CB), and acetonitrile (MeCN), respectively. These results are in agreement with a mechanism involving initial hydrogen abstraction and eliminate a mechanism involving initial electron transfer.

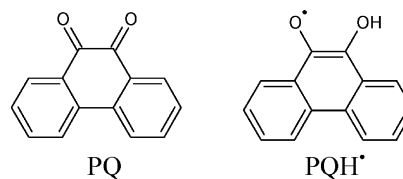
This same reaction was studied for the triplet of benzophenone. Values of k_H/k_D were 2.56, and 2.28, in CCl_4 , and MeCN, respectively. The rate of hydrogen abstraction was faster in MeCN than in CCl_4 . These results are explained considering a polar transition state which is stabilized by polar solvents.

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1. Introduction

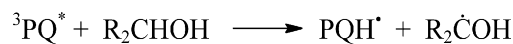
Light absorption by the *ortho*-quinone 9,10-phenanthrenequinone (PQ) efficiently generates a mixture of n,π^* and π,π^* triplets in thermal equilibrium [1]. The lowest energy triplet is n,π^* in carbon tetrachloride (CCl_4) but π,π^* in acetonitrile (MeCN) [1]. This coloured quinone is efficiently photoreduced by hydrogen donors including alcohols, aldehydes, ethers, esters, hydrocarbons, alkyl aromatics, and olefins containing allylic hydrogens [2–4]. The principal product is the corresponding hydroquinone 9,10-dihydroxyphenanthrene, or 1,4 and 1,2 addition products depending on the nature of the donor [3,4].



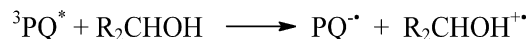
We have studied the photoreactivity of PQ with 2-propanol and it was shown that the n,π^* triplet is very reactive towards hydrogen abstraction from this alcohol in both CCl_4 and MeCN [2]. In CCl_4 , there is no measurable activation energy for this reaction, while in MeCN the activation energy was found to be equal to the energy difference between the lowest π,π^* and the higher n,π^* triplets [2]. We suggested that this high reactivity might be due to the high reduction potential of the quinone n,π^* triplet [2].

The photoreaction of ketones with primary and secondary alcohols is generally accepted to begin with alpha hydrogen abstraction by the n,π^* triplet carbonyl [5], and this mechanism is also proposed for PQ (Scheme 1) [6–10]. However, a mechanism involving initial electron transfer has also been proposed

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Scheme 1.



Scheme 2.

for quinones [3,4,11,12] including specifically PQ (Scheme 2) [13,14].

The mechanism involving initial hydrogen atom abstraction by excited PQ is based on laser flash photolysis experiments in which a transient identified as the PQ triplet is quenched by primary or secondary alcohols with the formation of a new transient attributed to the PQ semiquinone radical (PQH[•]) [6]. This was recently observed by Harada et al. [10] both for PQ and 1,2-naphthoquinone. However, initial electron transfer followed by rapid proton transfer would generate the same transients. It is therefore not possible to eliminate a mechanism involving initial electron transfer based only on the experiments reported in the literature until now.

In this paper, we present laser flash photolysis studies of the reaction of the PQ equilibrating triplets with 2-propanol and deuterated 2-propanol. Deuterium kinetic isotope effects were measured and compared with values also obtained for benzophenone for which the mechanism has been extensively studied. The results presented here clearly show that the initial photochemical process is abstraction of the alpha hydrogen atom in 2-propanol, and re-enforce the hypothesis that the high reactivity observed for PQ photoabstraction is due to the high reduction potential of the triplet n,π^* state of PQ.

2. Experimental

PQ (Aldrich 99+%), BP (Matheson, Coleman and Bell, analytical grade), 2-propanol-2-d (D, 98%, Cambridge Isotope Laboratories), and the solvents (UV grade), were used as received. Samples were deaerated by bubbling purified nitrogen for 5 min prior to analysis.

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 (5×10^{-4} M) and BP (2×10^{-3} M) had an average energy of 40 mJ and 5 ns pulse duration. Triplet–triplet absorption and phosphorescence emission were detected by a Hamamatsu R928 photomultiplier digitalized by a Tektronix TDS520 oscilloscope.

The decay of the PQ triplet as a function of the hydrogen donor concentration used in the Stern–Volmer plots was obtained from the emission at 580 nm in CCl₄ or CB (chlorobenzene), and from absorption at 680 nm in MeCN. The decay of the BP triplet was obtained from the emission at 452 nm in CCl₄ and at 444 nm in MeCN. The concentration of the hydrogen donor was varied by successive addition of a donor solution to the same sample by syringe and nitrogen bubbling. Each quenching experiment was carried out in a single session and under the

same experimental conditions. In each analysis it was used five laser pulses.

Room temperature steady-state phosphorescence spectra of BP (2.0×10^{-3} M) in CCl₄ and MeCN were obtained using a SPEX-Fluorolog 2 - Model F111X1 fluorimeter with photo-counting, in the right angle configuration. An excitation wavelength of 340 nm was used.

3. Results

3.1. 9,10-Phenanthrenequinone (PQ)

Laser flash photolysis of PQ at 355 nm with analysis of the decay of emission or triplet–triplet absorption gave rates of triplet decay as a function of 2-propanol-2-d concentration in three solvents, carbon tetrachloride, chlorobenzene (CB), and acetonitrile. These rates are compared with the rates for 2-propanol already published [2]. The results are presented as Stern–Volmer plots in Fig. 1. The time resolved phosphorescence [1] and triplet–triplet absorption [2] spectra of PQ have already been published.

The rate constants and kinetic deuterium isotope effects $k_{\text{H}}/k_{\text{D}}$ are presented in Table 1.

3.2. Benzophenone (BP)

The quenching of the benzophenone triplet by 2-propanol and 2-propanol-2-d was studied by following the time resolved emis-

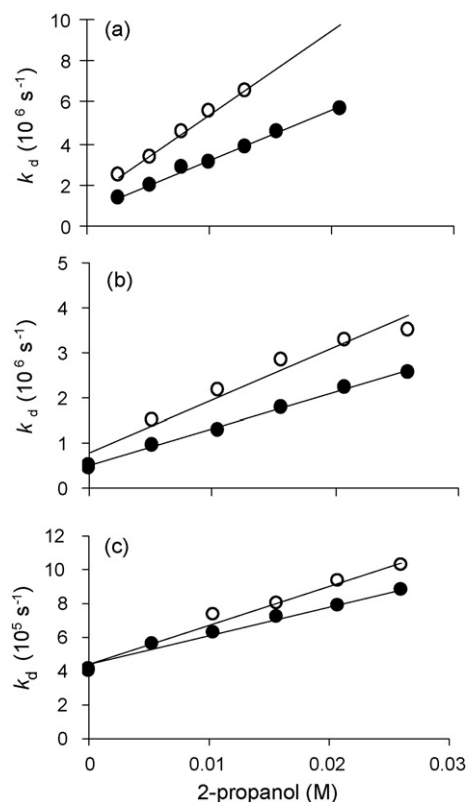


Fig. 1. Stern–Volmer plots of the rate of PQ triplet decay as a function of (○) 2-propanol and (●) 2-propanol-2-d concentration in (a) CCl₄, (b) CB and (c) MeCN.

Table 1
Deuterium isotope effects (k_H/k_D) on the rate of the reaction (k_H) of phenanthrenequinone triplet (PQ) and benzophenone triplet (BP) with 2-propanol and 2-propanol-2-d

Solvent	PQ k_H ($M^{-1} s^{-1}$) ^a	k_H/k_D	BP k_H ($M^{-1} s^{-1}$)	k_H/k_D
CCl ₄	$3.3 (\pm 1.1) \times 10^8$	1.69 ± 0.06	$1.95 (\pm 0.06) \times 10^6$	2.56 ± 0.11
CB	$1.2 (\pm 0.3) \times 10^8$	1.45 ± 0.16		
MeCN	$2.5 (\pm 0.8) \times 10^7$	1.36 ± 0.09	$3.17 (\pm 0.22) \times 10^6$	2.28 ± 0.16

^a Ref. [2].

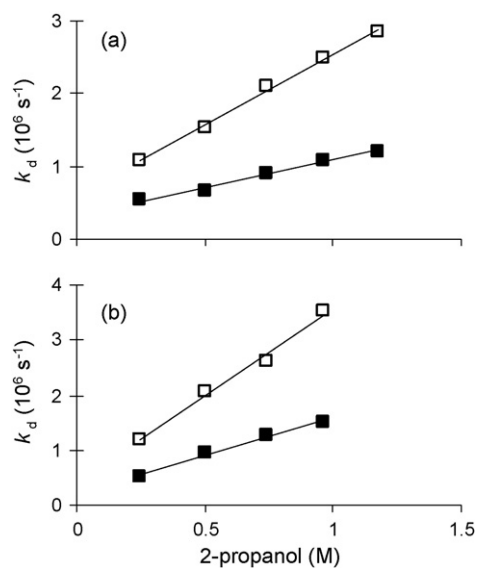


Fig. 2. Stern–Volmer plots of the rate of BP triplet decay as a function of (□) 2-propanol and (■) 2-propanol-2-d concentration in (a) CCl₄ and (b) MeCN.

sion decay in CCl₄ and MeCN. The resulting Stern–Volmer plots are shown in Fig. 2. The rate constants and kinetic deuterium isotope effects are presented in Table 1.

The value for the rate of quenching of BP by 2-propanol in MeCN determined here (Table 1) is in reasonable agreement with the value of $2.3 (\pm 0.3) \times 10^6 M^{-1} s^{-1}$ previously measured by laser induced time resolved emission decay at 435 nm [15]. No literature value for the rate of quenching of the BP triplet by 2-propanol in CCl₄ could be found, but the kinetic deuterium isotope effect in CCl₄ found in this study (Table 1) is close to the value of $k_H/k_D = 2.78$ found in benzene in 1964 using quantum yield measurements [16].

4. Discussion

4.1. Hydrogen abstraction versus electron transfer

The initial interaction between the PQ triplet and 2-propanol may involve either initial hydrogen atom abstraction (Scheme 1) [6–10], or initial electron transfer (Scheme 2) [13,14]. This question was resolved by the observation of a primary kinetic deuterium isotope effect in the three solvents studied (Fig. 1 and Table 1). The transition state must involve some breakage of the carbon–hydrogen (alpha) bond and a mechanism via hydrogen abstraction is confirmed (Scheme 1). Although the observed kinetic deuterium isotope effects are small (Table 1), they are

clearly primary considering that the reaction studied is the time resolved quenching of the PQ triplet.

4.2. Charge separation in the transition state

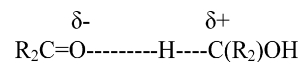
The values of the kinetic deuterium isotope effects are low for PQ and also for BP, which is a arch-typical ketone with a lowest n, π^* triplet known to react with 2-propanol by hydrogen abstraction [17,18]. These low values are an indication that in the transition state there is an asymmetric C–H bond breaking, and this asymmetry is of an “early” transition state. Since the n, π^* triplet carbonyl oxygen is electron deficient [5] and the non-bonding electron pairs of the alcohol oxygen contribute toward stabilization of the positive charge [19,20], a polar transition state is expected with charge transfer as shown in Scheme 3.

The effect of alpha deuteration of *sec*-butylamine on the rate of quenching of the benzophenone triplet had been studied and the authors found a small deuterium isotope effect ($k_H/k_D = 1.2$) and also concluded that hydrogen abstraction was occurring in a polar transition state [21].

A polar transition state for hydrogen abstraction as shown in Scheme 3 should be stabilized by polar solvents, leading to increased charge transfer, less stretching of the carbon–hydrogen bond and a smaller kinetic isotope effect [22]. The deuterium effect for PQ is greatest in CCl₄, less in CB, and smallest in MeCN (Table 1). The same was observed for BP in CCl₄ and MeCN (Table 1).

The smaller kinetic isotope effect observed for the PQ triplet relative to the BP triplet (Table 1) was also expected considering that the transition states are polarized. A larger degree of polarization of the transition state of the PQ triplet is expected relative to the BP triplet due to the greater reduction potential of the PQ triplet ($E_{red}^* = 33.6$ kcal/mol) relative to the BP triplet ($E_{red}^* = 27.1$ kcal/mol) [2].

Stabilization of the transition state due to the formation of a partial intramolecular hydrogen bond between the hydrogen of the donor and the two syn carbonyls has recently been proposed to explain the high reactivity of the PQ triplet [10]. The same explanation has previously been suggested by Scaiano et al. [23] to justify the high reactivity of 1,1,4,4-tetramethyl-1,4-dihydro-2,3-naphthalenedione. However, Wagner and Park [5] had commented that it is not clear that the energy gained by a partial hydrogen bond would be sufficient to offset the 13 kcal/mol



Scheme 3.

lower triplet energy of diketones relative to benzophenone. The present results indicate that the high reactivity of the n,π^* triplet of PQ is rather due to its large reduction potential as we have recently proposed [2].

4.3. The effect of solvent on the reactivity of n,π^* triplet ketones

The polarization of the transition state for the reaction of n,π^* triplet ketones with 2-propanol is well known [19,20]. It would therefore be expected that this reaction would proceed more rapidly in polar solvents than in non-polar solvents and that there would be a parallel between lower kinetic deuterium isotope effects and larger rate constants for reaction as the solvent polarity is increased, as long as the triplet remains n,π^* in nature. For the PQ triplet this increase could not be verified because the activation energy for reaction from the n,π^* state is essentially zero [2] in the solvents studied (CCl_4 and MeCN). The rate of reaction is controlled by the pre-exponential factor A which is essentially the same in both solvents [2]. The reaction of the PQ n,π^* triplet is already at its maximum rate in CCl_4 and cannot be faster in MeCN. The different rate constants shown in Table 1 are entirely due to differences in the population of the reactive n,π^* triplet in the two solvents [2].

The BP triplet is n,π^* in both polar and non-polar solvents [24,25]. In this study, the BP triplet was found to be more reactive toward hydrogen abstraction from 2-propanol in MeCN than in CCl_4 , with k_{H} being 1.6 times faster in MeCN than in CCl_4 (Table 1). Since the room temperature triplet energy obtained in the present work from room temperature phosphorescence spectra is 67.6 kcal/mol in both MeCN and CCl_4 (the same value had been found before in CCl_4 [26]) there is no difference in the triplet energy that could cause this difference in rate. For BP, an increase in solvent polarity causes an increase in the rate of hydrogen abstraction by the n,π^* triplet, as is expected due to better solvation by the more polar solvent for the polar transition state.

4.4. Final comments

The similarity in the photochemical reactivity of BP and PQ would seem to indicate that *ortho*-quinones such as PQ act typically as aromatic ketones and need not be considered a separate category, at least when hydrogen abstraction from alcohols is considered. The differences in reactivity are basically due to differences in the reduction potentials of the n,π^* triplets.

The reactivity of n,π^* triplet ketones in the reaction with hydrogen donors is often compared with the reactivity of alkoxy radicals [5]. Both are electrophilic and a polar transition state is invoked to explain their reactivity when abstracting the alpha hydrogen from alcohols. Thus, the results obtained in this study for the effect of solvent polarity on the kinetic deuterium isotope effects and rate of hydrogen abstraction were to be expected. However, it was surprising to find that this had not previously been described in the literature, and that it had been previously argued that solvent polarity had no effect on the rate of hydrogen abstraction from alcohols [25,27] and that the effect would be the

inverse of what was observed in this study [28]. The present work therefore provides for the first time an illustration of the effect of solvent polarity on the rate of alpha hydrogen abstraction from an alcohol by a n,π^* triplet ketone.

5. Conclusions

The results of our kinetic isotope effect study support a mechanism for the photoreduction of 9,10-phenanthrenequinone by 2-propanol which is initiated by the abstraction of the alpha hydrogen atom by the n,π^* triplet of PQ and not by electron transfer. A polar transition state with little hydrogen–carbon bond breaking (an early transition state) is in agreement with the experimental results. It is concluded that the high reactivity of PQ toward photoreduction is due to the high reduction potential of the n,π^* triplet. It is shown that the rate of hydrogen abstraction from 2-propanol by the benzophenone n,π^* triplet is greater in a polar than in a non-polar solvent, indicating that the polar transition state is stabilized by the polar solvent.

Acknowledgments

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