Influence of solvent polarity on the photoreactivity of 2–4-ring aromatic *o*-quinones

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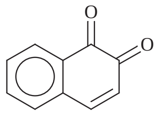
The solvent polarity dependence of the photoreactivity of naphthalene-1,2-dione (**1**), acenaphthylene-1,2-dione (**2**), phenanthrene-9,10-dione (**3**), and aceanthrylene-1,2-dione (**4**) was investigated by means of nanosecond laser-flash photolysis techniques. The reactivity of the triplets of **1**, **2**, and **3** towards hydrogen abstraction increases as the polarity of the solvent decreases owing to an inversion between n,π* and π,π* triplet states relatively close in energy. The relative increase in triplet reactivity follows the order **2** < **3** < **1**. In the case of **4** no inversion of triplet levels is detected; the lowest excited triplet state of **4** is π,π* in character in both polar and nonpolar solvents.

Introduction

In contrast to the case of *p*-quinones, there have been very few systematic studies on the photochemistry of *o*-quinones. Several *o*-quinones have been found to be photoreactive in the presence of hydrogen donors.[1–9] Furthermore, EPR and chemically induced dynamic electron polarization (CIDEP) investigations have shown significant solvent effects on the electronic character of the lowest excited triplet (T_1) states of *o*-quinones such as naphthalene-1,2-dione and phenanthrene-9,10-dione.[10] It has been demonstrated that the T_1 state of these two *o*-quinones has dominant π,π* character in ethanol matrices while it is n,π* in nonpolar media;[10,11] this inversion in triplet state character is the result of a small energy separation between the n,π* and π,π* triplet levels. Since ketones having low lying π,π* triplets are known to be substantially less reactive than those having low lying n,π* states,[12] one could anticipate that a decrease in solvent polarity should induce an increase in the photoreactivity of *o*-quinones. While this type of effect (*i.e.* solvent-induced inversion of triplet levels) is not unprecedented,[12,13] the magnitude of the concomitant change in the reactivity of *o*-quinones triplets is unknown.

In the present paper we report the results of a study of the influence of solvent polarity on the photoreactivity of *o*-quinones such as naphthalene-1,2-dione (**1**), acenaphthylene-1,2-dione (**2**), phenanthrene-9,10-dione (**3**), and aceanthrylene-1,2-dione (**4**) towards H-atom and electron transfer processes. These investigations show that, as the polarity of the solvent decreases, the relative reactivity of the triplets of **1**, **2**, and **3** increases in the order **2** < **3** < **1** . In the case of **4** no inversion of triplet levels is detected; the T_1 state of **4** is found to be π,π* in character in all media.



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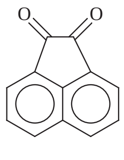

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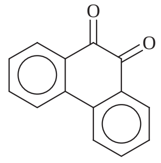

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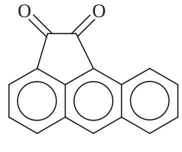

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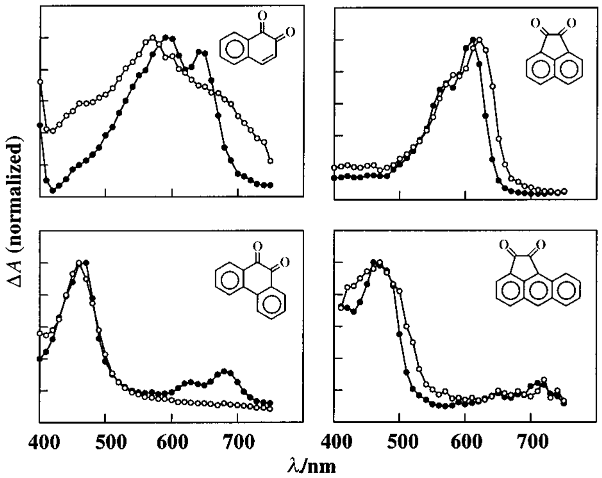


Fig. 1 Triplet–triplet absorption spectra recorded after 355 nm laser excitation of *o*-quinones in nitrogen-saturated acetonitrile (●) and benzene (○) solutions.

Results and discussion

The triplet–triplet (T–T) absorption spectra of all four *o*-quinones were recorded upon 355 nm laser excitation of nitrogen-saturated acetonitrile solutions as well as benzene solutions (Fig. 1). The observed T–T absorption bands for **1** and **3** in benzene solutions and for **2** in acetonitrile solution are in excellent agreement with earlier reports.[8,9] Both in the case of **1** and **3** there is a slight (*i.e.* $\Delta\lambda \le 20$ nm) bathochromic (red) shift of the wavelength of maximum absorption in acetonitrile as compared with that observed in benzene, while in the case of **2** there is a slight hypsochromic shift. Furthermore, the T–T absorption band of **1** observed in benzene is significantly wider than that in acetonitrile. These spectral changes are attributed to the effects of the media on the π,π*–n,π* triplet energy gap.

In all cases, and at low excitation doses, triplet decays having lifetimes in the order of several microseconds can be adequately fitted to first-order kinetics. At high excitation doses triplet lifetimes become shorter and involve a second-order component (a representative decay trace is shown in Fig. 2, inset). This observation is not unusual, and is ascribed to triplet–triplet annihilation. Such a process is found to be more significant in polar solvents where the triplets are longer lived. In the case of **4** (the least reactive of all four *o*-quinones under study, see below), the first-order rates observed at low excitation doses are found to be concentration dependent, a result which reflects self-quenching of the triplet (a rather common process, for

Table 1 Absolute rate constants for the reactions of acenaphthylene-1,2-dione, naphthalene-1,2-dione and phenanthrene-9,10-dione triplets with several H-donors in acetonitrile and benzene solutions[a]

Hydrogen donor	$k_Q/10^7$ M^{-1} s^{-1}					
	Acenaphthylene-1,2-dione		Naphthalene-1,2-dione		Phenanthrene-9,10-dione	
	Benzene	ACN	Benzene[b]	ACN	Benzene	ACN
Tetrahydrofuran	0.34 ± 0.01	0.15 ± 0.01	2.7 ± 0.1	0.090 ± 0.005	43 ± 1	3.5 ± 0.2
Diethyl ether	0.15 ± 0.01	0.080 ± 0.004	1.4 ± 0.1	0.030 ± 0.001	25 ± 2	1.3 ± 0.1
Propan-2-ol	0.090 ± 0.003	0.037 ± 0.001	0.66 ± 0.02	0.023 ± 0.001	16 ± 1	0.76 ± 0.02
Methanol	0.013 ± 0.005	0.0078 ± 0.0004	0.22 ± 0.01	0.0033 ± 0.0002	5.0 ± 0.2	0.21 ± 0.02
Benzhydrol	0.64 ± 0.03	0.13 ± 0.01	2.2 ± 0.1	0.10 ± 0.01	22 ± 2	1.0 ± 0.1
Cyclohexane	[c]	[c]	0.045 ± 0.002	[c]	0.64 ± 0.02	0.064 ± 0.003
Toluene	[c]	[c]	0.033 ± 0.006	[c]	0.58 ± 0.02	0.054 ± 0.007

[a] At 21 °C. [b] Solvent contains 1% acetonitrile. [c] Reaction was too slow to determine an accurate value.

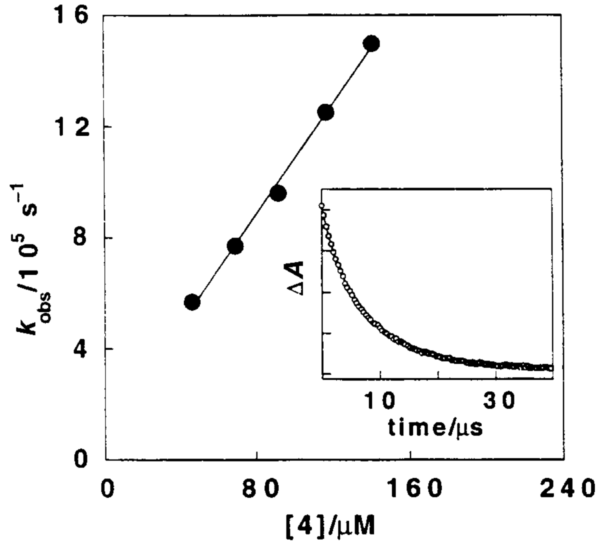


Fig. 2 Dependence of the observed pseudo-first-order component for the decay of **4** triplet as a function of the concentration of the precursor. Inset: triplet decay trace for 125 μM **4** monitored at 465 nm; trace was fitted with a combination of first and second order kinetics.

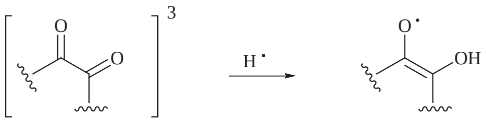
example, in long lived triplet ketones).[13] A plot of the observed first-order rates as a function of [**4**] yields k_{SQ}, the self-quenching rate constant from the slope (Fig. 2); in acetonitrile solution the resulting k_{SQ} value is (9.9 ± 0.4) × 10^8 M^{-1} s^{-1}.

In order to assess quantitatively the effect of solvent-induced inversion of triplet levels on the photoreactivity of *o*-quinones, the dynamics for the reactions of the triplets of **1**, **2**, **3**, and **4** with alcohols, ethers, hydrocarbons and amines were investigated in solvents of different polarity. Triplets of **1**, **2**, and **3** are found to be quenched by typical hydrogen donors (H-donors) such as methanol, propan-2-ol, benzhydrol, diethyl ether, tetrahydrofuran, cyclohexane and toluene. The pseudo-first-order rate constants, k_{obs}, determined experimentally from triplet decays in the presence of any of the above mentioned H-donors are related to the corresponding quenching rate constant k_Q according to eqn. (1), where k_o is the triplet decay rate constant

$$k_{obs} = k_o + k_Q[Q] \qquad (1)$$

in the absence of the H-donor, and [Q] is the concentration of the H-donor. Thus, values of k_Q were determined from the slope of linear plots (not shown) of k_{obs} *vs.* [Q]; the resulting values are summarized in Table 1. Comparison of such data shows that there is a considerable increase in triplet reactivity in benzene solutions as compared with that in acetonitrile solutions; triplet reactivity increases by a factor of *ca.* 3.5, 12, and 23 in the case of **2**, **3**, and **1**, respectively.

The reactions of the triplets of **1**, **2**, and **3** with the H-donors listed in Table 1 lead to the formation of semiquinone radicals (eqn. (2)); the residual transient absorption spectra (not shown)



(2)

obtained in the presence of these H-donors agree very well with data reported in the literature for these radicals, *e.g.* signals with maxima around 450 nm and 390 nm for **2**[9] and **3**,[2] respectively. An important factor in determining the rate of the reaction represented by eqn. (2) is the nature of the excited triplet state. As pointed out earlier, ketones having low lying π,π* triplets are known to be substantially less reactive than those having low lying n,π* states.[12] The increase observed in triplet reactivity as the solvent is changed from acetonitrile to benzene is consistent with a change in the nature of the low lying triplet excited state, *i.e.* from π,π* ('unreactive') to n,π* ('reactive') as previously reported.[10] As already mentioned, solvent effects increase in the order **2** < **3** < **1**; this observation could be interpreted as being a result of the π,π*/n,π* energy gap increasing in the order **1** < **3** < **2**. EPR studies in polar solvents have demonstrated that the T_1 states of **1** and **3** are π,π* in character while the triplet of **2** is n,π*.[10,11] The fact that both **1** and **3** triplets are found to be effectively reduced by typical H-donors in acetonitrile solutions indicates that, although the π,π* triplets can be expected to predominate, the photoreduction clearly involves n,π* triplets. Thus, both types of triplets are expected to be present as a result of an equilibration of triplet levels close in energy;[12] the n,π* character of the triplets increasing as the polarity of the media decreases. Comparison of data in Table 1 also shows that the n,π* triplet of **3** (which is expected to predominate in benzene solutions) is significantly more reactive than those of **1** and **2** in spite of the trend in triplet energy. The triplet state energy for **3** (48.8 kcal mol^{-1})[14,15] is higher than that predicted for **1**[8] but slightly lower than the energy reported for **2** (49.5 kcal mol^{-1}).[15] The higher reactivity of **3** is attributed to a more favorable enthalpy change as a result of resonance stabilization.

Triplets of **4**, on the other hand, do not react readily with any of the H-donors listed in Table 1. The lack of reactivity clearly indicates that the low lying triplet of **4** must be π,π* in character in both polar and nonpolar solvents, and that there is no n,π* triplet close in energy (*i.e.* large π,π*–n,π* energy gap).

Triplets of **1**, **2**, and **3** are also effectively quenched by amines such as triethylamine (TEA), a quencher that acts as an electron donor. The quenching rate constants determined according to eqn. (1) are all in the range (5–9) × 10^9 M^{-1} s^{-1}. Thus, k_Q values for reactions with TEA in acetonitrile and benzene are, respectively, (7.2 ± 0.2) × 10^9 M^{-1} s^{-1} and (6.8 ± 0.1) × 10^9 M^{-1} s^{-1} for **1**, (6.0 ± 0.1) × 10^9 M^{-1} s^{-1} and (4.7 ± 0.1) × 10^9 M^{-1} s^{-1} for **2**, and (8.2 ± 0.5) × 10^9 M^{-1} s^{-1} and (8.4 ± 0.4) × 10^9 M^{-1} s^{-1} for

Table 2 Absolute rate constants for the reduction of aceanthrylene-1,2-dione triplets by amines in different solvents[a]

	$k_Q/10^7\ M^{-1}\ s^{-1}$	
	Quencher	
Solvent	TEA	DABCO
Chloroform	0.060 ± 0.003	1.5 ± 0.1
Methanol	0.14 ± 0.01	11.4 ± 0.2
Acetonitrile	0.34 ± 0.01	366 ± 5

[a] At 21 °C.

3. Residual transient absorption spectra (not shown) indicate the formation of semiquinone radicals as well as of quinone radical anions; the latter are characterized by having absorption bands centered at 500–520 nm. The lack of solvent dependence of the reactions with TEA, particularly in the case of **1** and **3** triplets, is attributed to a compensating effect due to (i) the expected increase (in polar media) of the rate of the reaction involving charge separation in the transition state (as is indeed observed in the case of **2**), and (ii) the concomitant decrease in triplet reactivity as a result of an increase in π,π* character of the triplet.

Although triplets of **4** do not react with alcohols, ethers and hydrocarbons, these same triplets are efficiently reduced by amines such as TEA and 1,4-diazabicyclo[2.2.2]octane (DABCO). Photoreduction of **4** was studied in acetonitrile, methanol and chloroform. Quenching rate constants were determined according to eqn. (1), and resulting values are summarized in Table 2. Comparison of these k_Q values indicates that rate constants for the reduction of **4** triplets decrease as the polarity of the medium also decreases, observations which are consistent with charge transfer processes. In fact, reactions with DABCO must be electron transfer processes since DABCO has no easily abstractable hydrogens due to unfavorable stereoelectronic effects. Also, it is found that the reactivity of **4** triplets towards TEA is significantly lower than that of **1**, **2**, and **3** triplets. The lower reactivity of **4**, as pointed out earlier, is in agreement with a low lying triplet state π,π* in character.

In summary, owing to a small π,π*–n,π* energy gap and concomitant increase in the n,π* character of the triplet as the solvent is changed from acetonitrile to benzene, the photoreactivity of **1**, **2** and **3** towards H-abstraction increases by a factor of *ca.* 3.5, 23 and 12, respectively. The trend observed in the relative change in triplet reactivity is ascribed to the π,π*–n,π* energy gap increasing in the order **1** < **3** < **2**. No solvent effects could be detected on the nature of the lowest lying triplet state of **4**; the observed triplet behaviour is consistent with T_1 being π,π* in character in all media.

Experimental

Aceanthrylene-1,2-dione, acenaphthylene-1,2-dione, naphthalene-1,2-dione, phenanthrene-9,10-dione, benzhydrol (Aldrich) and DABCO (BDH) were recrystallized before use. Triethylamine (Aldrich) and diethyl ether (BDH) were distilled before use. Acetonitrile, benzene, chloroform, cyclohexane, methanol, propan-2-ol, tetrahydrofuran, and toluene (BDH, Omnisolv grade) were used as received.

Laser experiments were carried out using a Q-switched Nd/YAG laser (Continuum, Surelite I) operated at 355 nm (4–6 ns pulses, < 20 mJ pulse^{-1}) for excitation. The system is controlled by a Power Mac 7100/80 computer running LabView 3.1.1 from National Instruments. This computer is interfaced (GPIB) to a Tektronix TDS 620 A digitizer used for data acquisition. Further details on this laser system have been reported elsewhere.[16,17] Solutions were contained in quartz cells constructed of 7 × 7 mm^2 Suprasil tubing. All samples were deaerated by bubbling oxygen-free nitrogen for 20 minutes. Transient absorption spectra were collected under flow conditions in order to minimize substrate depletion. All measurements were carried out at room temperature, *i.e.* (21 ± 1) °C.

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