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Photochromism and Kinetics of Naphthacenequinones

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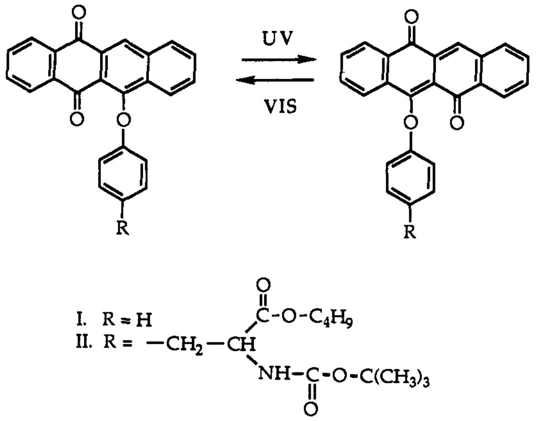
Abstract: The photochemistry and the irreversible photodecomposition of naphthacenequinones have been studied. Picosecond, nanosecond, and longer lived transient spectra have been recorded and the kinetics of the intermediates measured and assigned to specific transient species. On the basis of the data, a mechanism for the photoinduced structural rearrangement is proposed. The adiabatic reaction is found to proceed via triplet states and the irreversible decomposition due to excited triplet abstraction of hydrogen from the solvent.

Photochromism is an area which has been continuously growing in importance and therefore research activity because of its interesting photochemistry and the potential application of these materials to electronic and other devices. The most extensively studied class of photochromic materials are spiropyrans. Their photochemistry, kinetics, spectra, and photoinduced structural transformation have been described in some detail previously.[1-5]

The mechanism of photochemistry and spectroscopy of photochromic naphthacenequinones has been studied much less than that of the spiropyrans. The synthesis[6,7] and luminescence spectra[8,9] of only a few photochromic naphthaquinones have been published. Otherwise, there is very little information regarding this interesting class of photoactive materials. It has been proposed, however, that the photochromism of the photoactive naphthacenequinones is based on their photoisomerization to the *ana*-form.[6-10] The only related study which has been published recently[11-15] concerns the photochromic properties of anthraquinones. A feature which distinguishes the naphthacenequinones from the anthraquinones and spiropyrans is the absence of the back-thermal-reaction which is responsible for the instability of the colored form of the anthraquinones and spiropyrans.[16] This feature, namely the stability of both photochromic forms, suggests that photochromic naphthacenequinones may be suitable for use as materials for optical devices and possibly for storing information in 3D optical memory devices. For a material to be considered as a candidate for 3D memory, it should exhibit stability in both states, be photoerasable, i.e., capable of returning to the original form by excitation at a specific wavelength, and be read nondestructively by means of fluorescence. This means that spontaneous reversibility to the original form or decomposition from the excited state of the original or second form should be very small and practically nonexisting.[17-19]

Scheme 1. Photochromic Transformation of Naphthacenequinone



In this paper, we report our studies on the spectra and kinetics of the transient states leading to photochromism and, on the basis of these data, we propose a mechanism for the structural rearrangement and the photochemistry of naphthacenequinone molecules in general.

Experimental Section

The synthesis of compounds I and II (Scheme 1) has been presented previously.[20] The solvents used for our experiments were toluene (analytical grade), tetrahydrofuran (THF), methyltetrahydrofuran (methyl-THF) for low-temperature studies, and benzene. Absorption and fluorescence spectra were measured on a Cary 2200 spectrophotometer or a Shimadzu UV 160U spectrophotometer and a Shimadzu FR5000U spectrofluorophotometer. The excitation light sources were either a 100-W medium-pressure mercury lamp or a 100-W tungsten–iodine lamp for slow reactions, a mode-locked Nd/YAG laser for picosecond kinetics, and a N_2-pumped dye laser for nanosecond studies. Appropriate light filters and monochromators were used to isolate the excitation wavelengths at 313, 366, and 405 nm. Determination of the photon flux was achieved

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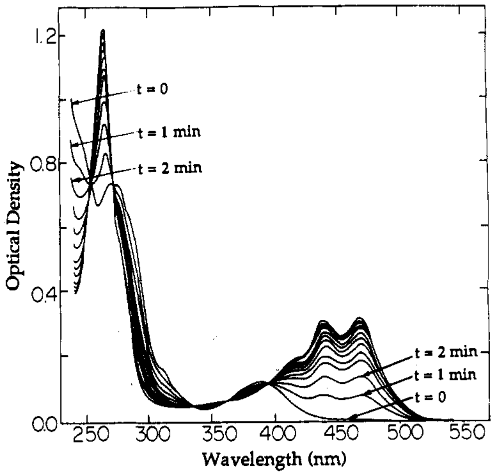

Figure 1. Absorption spectra of II in toluene at 23 °C. The curves represent the absorbance changes as a function of irradiation (λ = 405 nm) exposure time at 1-min intervals.

by actinometric methods: An accurately measured volume (V) of an Aberchrome 540 solution in toluene at a concentration sufficient to absorb all the incident radiation was exposed to UV light. This solution was placed in a 1-cm optical path cell and irradiated with 316–366-nm light for an accurately known period of time, t. After time t, the increase in optical density ΔD at 494 nm (the maximum of the long-wavelength absorption band of Aberchrome 540) was measured.[21] The photon flux I_0 may then be calculated from the expression:

$$I_0 = \Delta D_{\mathrm{Act}} V N / \varphi_{\mathrm{Act}} \epsilon_{\mathrm{Act}} l$$

where N is Avogadro's number, φ_{Act} is the quantum yield for the photocoloration of Aberchrome at 540 nm (0.20 for irradiation at 366 nm in toluene), ϵ_{Act} is the molar extinction coefficient of the colored form of Aberchrome (8200 dm^3 mol^{-1} cm^{-1} at 494 nm for the toluene solution), and l is the optical path length.

The time-resolved experiments were performed with a Nd/YAG picosecond laser and a N_2-pumped dye laser. The picosecond experimental system used for the investigation of the transient absorption spectra and kinetics has been described previously.[19] A passive/active-mode-locked Nd$^+$/YAG laser which emits 1064-nm, 25-ps pulses at a repetition rate of 20 Hz provided the laser excitation. The spectra were dispersed using a 0.25-m polychromator coupled to an OMA system. The energy of the beam was continuously monitored to ascertain that no saturation occured during these studies.

The nanosecond absorption spectra were measured with a N_2-pumped dye laser. The spectra were dispersed and recorded by a Jarrell-Ash monochromator and recorded by means of a photomultiplier coupled to a Tektronix 2430A digitizer followed by on-line computer processing.[22]

Quantum Yields and Steady-State Kinetics

Solutions of I and II in degassed benzene, toluene, and i-PrOH were irradiated at 405 and 366 nm. The irradiation produced the colored form, B, of I and II, respectively, which is shown in Figure 1. These colored forms have their absorption in the region of 410–500 nm, are stable, and do not revert to the original form at room temperature. The thermal stability of both forms, original, A, and colored, B, is an important property of naphthacenequinones which is absent in the case with spiropyrans where the merocyanine form undergoes thermal back-reaction at room temperature.[1] The back-reaction can be initiated photochemically by irradiation of the colored form of the naphthacenequinones at 420–520 nm. Prolonged irradiation, several hours, of solutions of I and II, however, was found to generate irreversible decomposition products when either $R = 1$ or $R = 2$ was used.

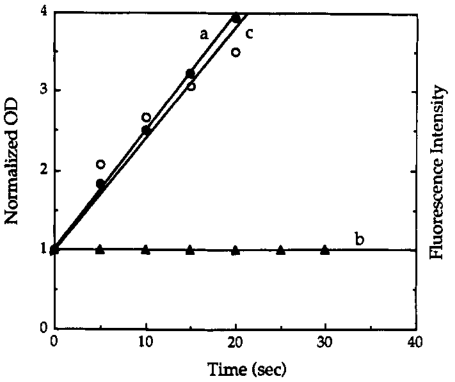

Figure 2. Normalized O.D. vs t for I in toluene measured at 480 nm and at the isobestic point at 395 nm shown as lines a and b, respectively. Line c is a plot of relative fluorescence intensity as a function of time measured at $\lambda_{\max} = 540$ nm, $\lambda_{\mathrm{exc}} = 480$ nm.

The rate of decomposition was found to be much faster in i-PrOH than in toluene solutions, which suggests that if the irreversible photodecomposition of I in toluene, due to irradiation at 405 nm, is neglected, the general scheme of the phototransformation can be simplified and described as:

$$\mathrm{A} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} \mathrm{B} \tag{1}$$

Under continuous irradiation, the change in concentration of the photoinduced form B is given by:[23]

$$\mathrm{d[B]}/\mathrm{d}t = I_0[\varphi_{\mathrm{B}}\epsilon_{\mathrm{A}}\mathrm{f}(D)[\mathrm{A}] - \varphi_{\mathrm{A}}\epsilon_{\mathrm{B}}\mathrm{f}(D)[\mathrm{B}]] \tag{2}$$

where φ_{B} and φ_{A} are quantum yields of the photoprocess A → B and B → A, respectively, ϵ_{A} and ϵ_{B} are the extinction coefficients of A and B at the irradiation wavelength, and f(D) and D are defined as

$$\mathrm{f}(D) = (1 - 10^{-D})/D;\ D = \epsilon_{\mathrm{A}} l[\mathrm{A}] + \epsilon_{\mathrm{B}} l[\mathrm{B}]$$

Equation 2 can be integrated only under the conditions that the optical density of the solution at the excitation wavelength does not change its value during the time of illumination. Figure 1 shows that this condition is fulfilled at the ~365- and ~395-nm isobestic points. Under irradiation with 366-nm light and the low conversion efficiencies of A to B, eq 2 can be solved as:

$$\varphi_{\mathrm{B}} = [\mathrm{B}]/(I_0 t\mathrm{f}(D) C_0 \epsilon_{\mathrm{A}})$$

where C_0 is the concentration at zero time. It can be seen from Figure 2 that a linear dependence exists between D_{B} and t, which suggests that the quantum yield φ_{A} can be determined from the data shown in Figure 1.

Continuous irradiation of form B by visible light induced also irreversible decomposition. This irreversible decomposition is found, as in the previous case, to be much faster in i-PrOH than in toluene solution. These results are shown in Figure 3. The rate of photocoloration of I and II in the presence of a small concentration of i-PrOH follows a linear dependence as a function of time. In pure i-PrOH, however, a chain reaction takes over and the change in optical density occurs after the irradiation has stopped. Form B fluorescence does not originate from the *ana*-form of B because UV light irradiation of the photoinduced form B leads to an increase in the fluorescence intensity. Belaits et al.[10] have attributed this fluorescence to the 11-hydroxy-5,12-naphthacenequinone—which is the product of the irreversible decomposition of I. Photodecomposition of both compounds is found to be accompanied by an increase in the fluorescence intensity of the products, and this intensity was found to be a

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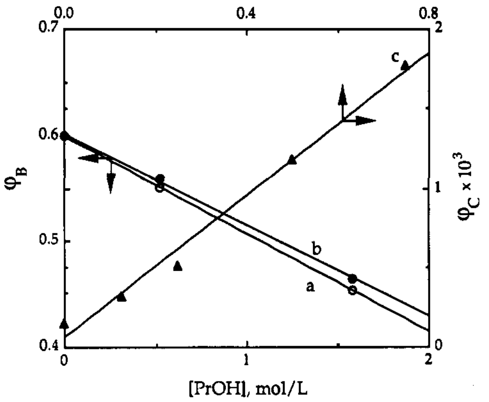

Figure 3. Dependence of quantum yield φ on added concentration of i-PrOH in solutions of I and II in benzene: (a) φ_B for the reaction A → B of I, (b) φ_B for reaction A → B of II, and (c) φ_C for the irreversible decomposition of I.

Table 1. Quantum Yields (φ_B) of Photochromism and Irreversible Photodecomposition (φ_C) of Compounds I and II in the Presence of Oxygen

n	solvent	λ_{exc} (nm)	ϵ_B (M^{-1} cm^{-1})	φ_B	φ_C
II	benzene	313	5.40×10^3	0.6 ± 0.1	0.00052 ± 0.0001
II	benzene	366	(455 nm)	0.6 ± 0.1	0.00034 ± 0.0001
II	benzene	405		0.58 ± 0.1	0.00021 ± 0.00006
II	i-PrOH	313		0.45 ± 0.1	0.0069 ± 0.0001
II	i-PrOH	366		0.4 ± 0.1	0.0026 ± 0.0001
II	i-PrOH	405			
I	benzene	347	1.7×10^4 [a]	0.6[b]	
I	benzene	366	(480 nm)	0.6 ± 0.1	0.00014
I	i-PrOH	366		0.5 ± 0.1	0.0035 ± 0.0005

[a] Taken from ref 6, chloroform. [b] Take from ref. 7.

linear function of irradiation time. The photoinduced formation of the fluorescing product, which strictly follows the irreversible decomposition of I and II, provides a more sensitive means for investigating the process of decomposition. This data also show that the quantum yield of the photodecomposition is linearly dependent on the incident-light intensity. These facts indicate that the decomposition is not the result of secondary photochemistry of B form but that the decomposition can compete with the main photochromic reaction which results in the structural transformation of the molecule which is responsible for the characteristic photocoloration observed in these materials. Quantum yields of photocoloration and irreversible decomposition are listed in Table 1. Quantum yields for the formation of the benzospiropyran merocyanine form have been reported earlier.[24]

Photochemical Reactions and Transient Kinetics

(a) Picosecond Excitation. Solutions of I and II in toluene and in i-PrOH were irradiated with 355-nm, 25-ps pulses. The time-resolved, from 0 to 17 ns, absorption spectra, obtained in the 300–600-nm region, following 355-nm excitation of I and II are shown in Figures 4 and 5. Figure 4 displays the picosecond transient spectra of compound I while Figure 5 shows the same as Figure 4 but for compound II. Figure 5 shows the absorption spectrum of a transient species, which was formed immediately after the excitation. The absorption band located at ~380 nm decays with a fast rate during the first 75 ps. Analysis of Figure 5a data makes it obvious that the primary absorption ($\lambda_{max} \simeq$ 380 nm) decreases while the red-shifted secondary absorption band ($\lambda_{max} \simeq$ 500 nm) grows simultaneously with the same rate. The rise-time kinetics at the 500-nm band is plotted in the form of O.D. vs time in Figure 5c. In order to investigate the kinetic behavior of the transients produced by the excitation of I and II, their absorption intensities changes were measured as a function of time. A plot of the change in intensity of the transient vs *t*, Figures 4b and 5b, shows the decay of the secondary absorption band intensity ($\lambda_{max} \simeq$ 500 nm) at various time intervals between 0.1 and 14 ns. The formation and decay of the transient states of I are plotted in Figure 4c.

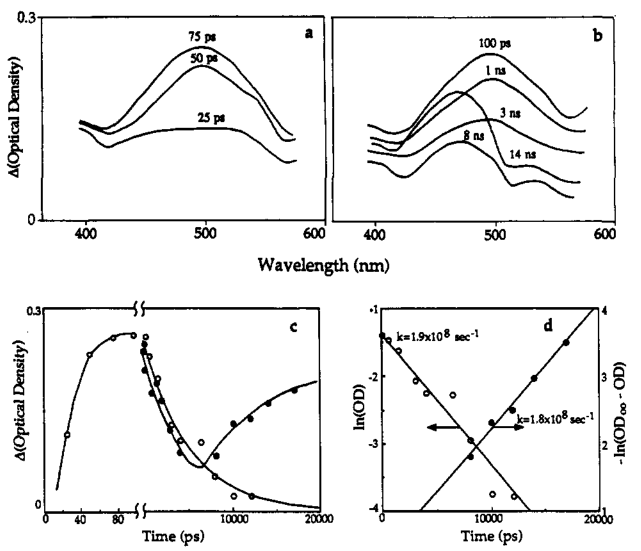

Figure 4. Time-resolved transient absorption spectra and kinetics of I in toluene (4×10^{-4} M) excited with a 25-ps, 355-nm pulse: (a) and (b) transient spectra, (c) open circles, kinetics measured at 500 nm, and closed circles, kinetics measured at 460 nm, and (d) rates of decay and formation from data in Figure 4c.

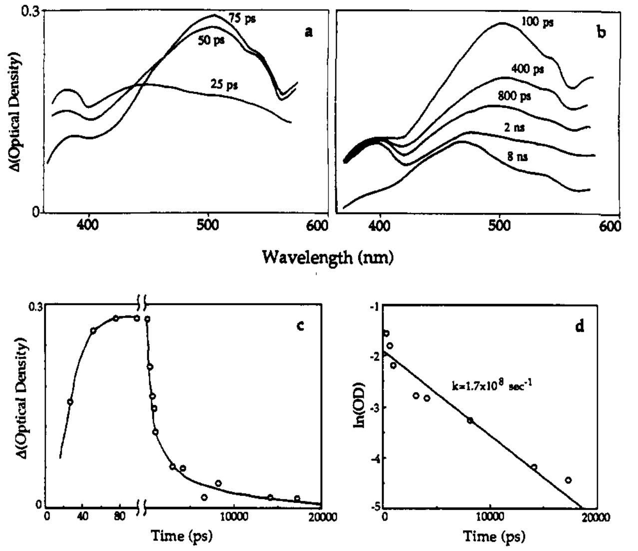

Figure 5. Same as Figure 4, for compound II.

When a solution of I in i-PrOH was irradiated with 355-nm pulses, we observed that the decay rate of the secondary absorption band ($\lambda_{max} \simeq$ 500 nm) became much faster in comparison to the rate of I in toluene. These data are shown in Figure 6.

(b) Nanosecond Excitation. When a deoxygenated solution of I in toluene was excited with 8-ns pulses, we found that a transient species, with an absorption spectrum which has its $\lambda_{max} \simeq$ 400 and 460 nm, was formed within the 8-nm time period of the excitation pulse. Time-resolved spectroscopy revealed a decrease in the 400-nm absorption band intensity (Figure 7a,b) which was also accompanied by a rise in the absorption of a photoinduced stable product of I; see Figure 7c,d. The absorption at 470 nm is assigned to the photoinduced *ana*-form of I because it is stable and has the same spectrum as the *ana*-form. The changes in the spectra of the intermediate form occuring immediately after excitation with a nanosecond pulse and 50 μs after excitation are displayed in Figure 8.

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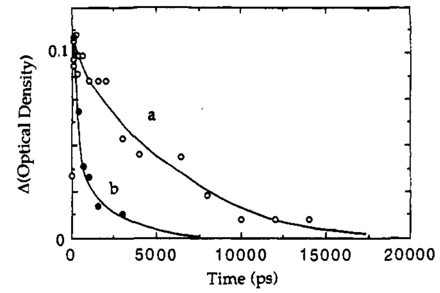


Figure 6. ΔO.D. (λ = 500 nm) vs time for the transient **IA** in toluene and isopropyl alcohol, curves a and b, respectively.

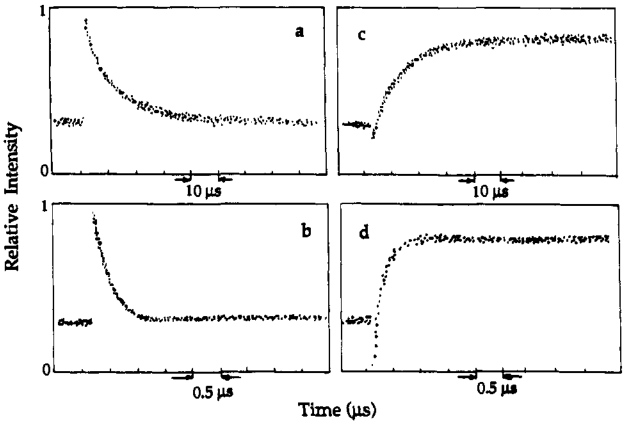


Figure 7. Time dependence of the transient absorption of **I** in toluene: (a) λ = 400 nm, without oxygen, (b) λ = 400 nm, with oxygen, (c) λ = 470 nm, without oxygen, and (d) λ = 470 nm, with oxygen.

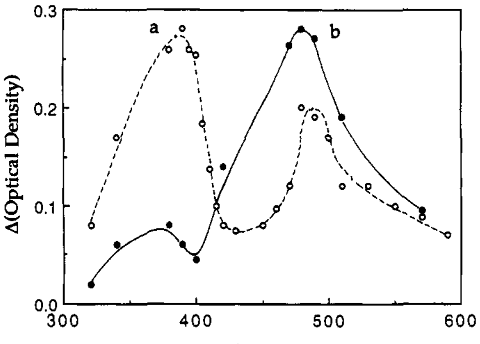


Figure 8. Triplet–triplet absorption spectra of **I** in toluene (a) immediately after nanosecond excitation and (b) 50 μs after excitation.

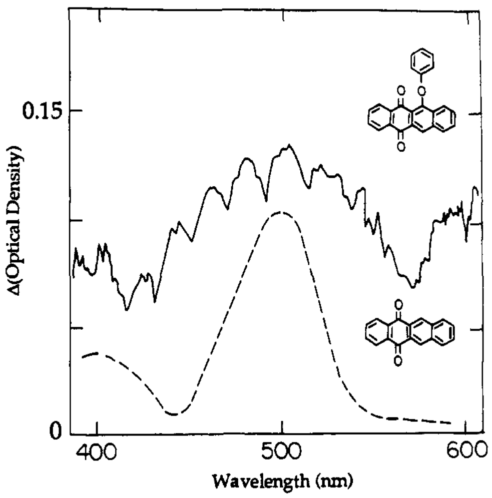


Figure 9. Transient absorption spectra of **II** and 5,12-naphthacenequinone in toluene after excitation with a nanosecond pulse.

In the presence of oxygen, the decay time constant of the first transient and the rise time of the *ana*-form become respectively faster, but the quantum yield of the photoinduced form remains the same as it was in the absence of oxygen. These data are shown in Figure 7.

Pulse excitation of **IB** and **IIB** in toluene with visible light leads to the same transient with $\lambda_{max} \simeq$ 400 nm, and its decay rate is also found to be increased by the presence of i-PrOH. The triplet–triplet absorptions of **I** and a similar but nonphotochromic molecule are shown for comparison in Figure 9.

Discussion

On the basis of our kinetic, time-resolved spectroscopic data and the information available in the literature, we have been able to assign the time constants we have measured to specific processes and the transient spectra to specific intermediate species. These assignments allow us to propose a most probable mechanism for the photochemical reactions leading to the formation of the *ana*-form of the naphthacenequinones studied. If we start the analysis of the mechanism by considering the final stable product, B, we propose the following.

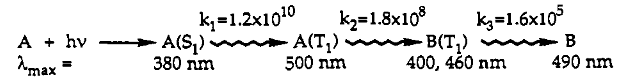
The stable *ana*-form of **I** could be formed from the transient species with $\lambda_{max} \simeq$ 400 nm. This precursor of **IB** is a triplet: it has a lifetime of about 30 ms in the absence of oxygen, and it is quenched by oxygen. However, the quantum yield of B does not depend on the concentration of oxygen. This statement is based on both the quantum yields and the kinetic data shown in Figure 7. Therefore, the precursor of B, whose spectrum has a $\lambda_{max} \simeq$ 400 nm, must be the triplet state of B. Subsequently, the quenching of this triplet state leads to the ground state of B. Gritsan et al.[13] have reported a similar triplet precursor for pery-(acyloxy)-9,10-anthraquinones. Direct excitation of B induces a triplet-state population which leads to the observed triplet–triplet absorption of B. The molecules in the triplet state B may then interact with i-PrOH to abstract an H-atom.

The triplet state of B could also be formed from its singlet state or, in fact, from another triplet state. As can be seen from Figure 4, the transient species with $\lambda_{max} \simeq$ 400 and 460 nm is formed from the secondary transient with a rate constant ~1.8×10^8 s^{-1} and an absorption spectrum with $\lambda_{max} \simeq$ 500 nm.

The next task is to analyze the nature of this transient species whose spectrum is characterized by an absorption band with $\lambda_{max} \simeq$ 500 nm. This spectrum coincides with that of the triplet–triplet absorption of the nonphotochromic 5,12-naphthacenequinone[7] in the same solvent (Figure 9). The time-resolved spectra plotted in Figure 5 show the spectra of the singlet state of **II** recorded 75 ps after excitation. The decay of the 380-nm band, of compound **II**, corresponds to the population decay of the singlet $(A)S_1$ to the triplet $(A)T_1$ (λ_{max} = 500 nm) which proceeds with a lifetime of 8.3×10^{-11} s. The triplet state of A decays to the triplet state of the B form, $(B)T_1$ (λ_{max} = 400 and 460 nm), with a lifetime of 8.3×10^{-9} s. The B-form triplet decays into the final product B with a lifetime of 6.3×10^{-6} s.

It is quite reasonable, therefore, to assume that the transient with $\lambda_{max} \simeq$ 500 nm is the triplet state of A, i.e., the initial quinoid form of **I** and **II**. This triplet state is capable of abstracting a hydrogen atom from i-PrOH because the decay of this triplet is accelerated in i-PrOH. The process by which a triplet state of A is formed, with a rate constant of 1.2×10^{10} s^{-1}, actually represents the intersystem-crossing rate in A.

On the basis of our kinetic data, the most probable mechanism for the formation of the photochromic product, induced by the 355-nm excitation of **I** and **II**, may be represented as follows:



$$\begin{array}{lccccccc} A + h\nu & \longrightarrow & A(S_1) & \xrightarrow{k_1=1.2\times10^{10}} & A(T_1) & \xrightarrow{k_2=1.8\times10^{8}} & B(T_1) & \xrightarrow{k_3=1.6\times10^{5}} B \\ \lambda_{max} = & & 380\text{ nm} & & 500\text{ nm} & & 400, 460\text{ nm} & \quad 490\text{ nm} \end{array}$$

We may propose, therefore, that the photoisomerization reaction of photochromic naphthacenequinones **I** and **II** is an adiabatic photoreaction proceeding via the triplet state. Examples of similar types of adiabatic photoreactions for 1-(acyloxy)-anthraquinones and for photoenolization have been reported previously.[11–15,25–27]

The existence of triplet ketone intermediates suggests that H-atom abstraction could compete efficiently with the photochromic reactions.

It follows from the above scheme that the formation of B ($\varphi_B = 0.6$) is directly related to the decay of $B(T_1)$. However, the H-atom abstraction could also compete with the photochromic reaction 3. Steady-state experiments show that in the presence of i-PrOH, the quantum yield of the photochromic reaction decreases and the quantum yield of the irreversible photodecomposition reaction of B increases. In terms of this scheme (see below), it is reasonable to assume that the irreversible photodecomposition is driven by triplet-B-state H-abstraction.

$$B(T_1) \rightarrow B(S_o) \qquad (3)$$

$$B(T_1) + \text{i-PrOH} \rightarrow BH^{\bullet} + (CH_3)_2COH^{\bullet} \text{ irreversible decomposition} \qquad (4)$$

$$B(T_1) + O_2 \rightarrow B(S_o) \qquad (5)$$

$$B(T_1) + RH \rightarrow BH^{\bullet} + R^{\bullet} \qquad (6)$$

Reaction 6 represents the irreversible decomposition by hydrogen abstraction from the solvent.

Using the above reaction scheme for the addition of i-PrOH, we can write the following expression which relates the quantum yield of the photochromic reaction with the concentration of i-PrOH.

$$(\varphi_B)_o/\varphi_B = 1 + \tau_B k_4[\text{i-PrOH}]$$

where $(\varphi_B)_o$ and φ_B are the quantum yields of photocoloration in the absence and in the presence of i-PrOH and τ_B is the lifetime of the lowest triplet state $B(T_1)$. A plot of φ_B vs [i-PrOH], shown in Figure 3, suggests that they are linearly related. We also found that $k_4 = (5.1 \pm 0.6) \times 10^4$ M^{-1} s^{-1} for compound **II** in benzene. Time-resolved experiments confirm these results because they give the rate constant for the direct quenching of $B(T_1)$ by i-PrOH as $(9.3 \pm 0.7) \times 10^4$ M^{-1} s^{-1}. It was previously suggested that the rate constant of H-abstraction from benzene is less than 10^3 M^{-1} s^{-1}.[28]

Considering this scheme, the following relationship is proposed for the quantum yield of the irreversible decomposition:

$$\varphi_B/(\varphi_C)_o = [k_4[\text{i-PrOH}] + k_6[RH]]/[k_6[RH]\tau_B(1/\tau_B + k_4[\text{i-PrOH}])]$$

Assuming that $k_6[RH] = 139$ s^{-1}, in benzene we obtain $k_4 = (4 \pm 1) \times 10^3$ M^{-1} s^{-1}. The lower value for the decomposition compared to the photocoloration data plotted in Figure 3 can be explained by the partial reversibility of reaction 4.

Therefore, the largest rate constant possible under this scheme for the H-atom abstraction by $B(T_1)$ of **II** in benzene is $(9.3 \pm 0.7) \times 10^4$ M^{-1} s^{-1}. Such low rate constants for H-abstraction from i-PrOH are characteristic of a triplet π,π^*-state.[29] The rate constant of the H-atom abstraction by $A(T_1)$ of **II**, as estimated from Figure 6, is found to be more than 1.3×10^8 M^{-1} s^{-1}, which is characteristic of a triplet n,π^*-state. On the basis of this kinetic and spectroscopic data, the lowest triplet state may therefore be assigned to n,π^* in 5,12-naphthacenequinone form A and π,π^* in form B.

In summary, time-resolved spectra and kinetic data have made it possible to assign the spectra of the intermediate species, measure the formation and decay of the transient states of naphthacenequinones, and propose a mechanism for the reactions and photochemistry responsible for the photochromism of these materials. These materials are important because they hold a promise for use in electronic switching and computer memory devices. This aspect of our research with these materials will appear shortly in another communication.

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