# Identification of Photoexcited Singlet Quinones and Their Ultrafast Electron-Transfer *vs* Intersystem-Crossing Rates

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**Abstract:** Photoexcitation of chloranil (**CA**) produces initially the excited singlet state $^1$**CA**\*, as demonstrated for the first time by time-resolved spectroscopy on the femtosecond/picosecond time scale. Electron transfer from aromatic donors (D) to singlet chloranil leads to short-lived (*ca.* 5 ps) singlet radical-ion pairs, $^1$[D$^{•+}$, **CA**$^{•−}$]. This ultrafast quenching process competes with intersystem crossing ($k_{ISC} \approx 10^{11}$ s$^{-1}$) to generate the triplet excited state, $^3$**CA**\*. The follow-up electron transfer from D to $^3$**CA**\* yields triplet radical-ion pairs, which are distinguished from their singlet analogues by their long (nanosecond) lifetimes. The competition between electron transfer and intersystem crossing on the early picosecond time scale also pertains to a wide variety of other photoexcited quinones related to chloranil. Electron transfer to singlet quinone as established here adds a new dimension to the generally accepted mechanisms which proceed from the triplet state, and the inclusion of reactions on both the triplet and the singlet manifolds provides a complete picture of photoinduced electron transfer to various quinone acceptors.
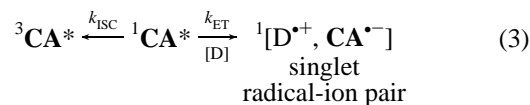
## Introduction

The role of quinones as electron and hydrogen-atom acceptors has been well established in a wide variety of chemical transformations.[1,2] In particular, the prototypical quinone chloranil (**CA**, tetrachloro-1,4-benzoquinone) is frequently employed in thermal and photoinduced electron-transfer reactions.[3−5] In thermal reactions, it is a one-electron oxidant with a reduction potential of $E_{red} = +0.02$ V *vs* SCE.[6] In photochemical applications, **CA** acts as a versatile sensitizer which commonly unfolds its electron-transfer reactivity from the lowest excited triplet (T$_1$) state.[3] Triplet chloranil ($^3$**CA**\*) exhibits a reduction potential of $E^*_{red} = 2.15$ V *vs* SCE,[7] and thus readily oxidizes electron donors (D) such as arenes,[4] alkenes,[4] amines,[4] alcohols,[5] etc. As a result, a reactive triplet radical-ion pair is generated by electron transfer, *i.e.*

$$^3\mathbf{CA}* + \mathrm{D} \rightarrow \ ^3[\mathbf{D}^{•+}, \mathbf{CA}^{•−}] \qquad (1)$$
$$\text{triplet} \atop \text{radical-ion pair}$$
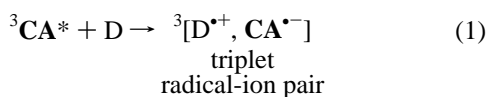
Since the electron transfer in eq 1 represents the crucial step in most photochemical transformations of chloranil it is classified as a triplet (electron-transfer) sensitizer. As a consequence, most photophysical and photochemical studies of chloranil relate to the *triplet* excited state, and little is known about its precursor, the excited *singlet* state. We therefore focussed our attention on the singlet manifold of the photoexcited quinone, and in particular on the lowest excited singlet state (S$_1$), its spectral features, its lifetime, and its reactivity. For instance, since singlet excited chloranil ($^1$**CA**\*) is expected to be an even better oxidant than triplet chloranil,[9] electron transfer within the singlet manifold leading to singlet radical-ion pairs may be observed, *i.e.*

$$^1\mathbf{CA}* + \mathrm{D} \rightarrow \ ^1[\mathbf{D}^{•+}, \mathbf{CA}^{•−}] \qquad (2)$$
$$\text{singlet} \atop \text{radical-ion pair}$$
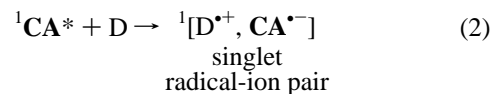
Since intersystem crossing to the triplet manifold competes with the electron transfer in eq 2, the overall electron-transfer reactivity of the quinone (singlet *versus* triplet) will depend on the relative rates of intersystem crossing ($k_{ISC}$) and electron transfer ($k_{ET}$) in eq 3:

$$^3\mathbf{CA}* \xleftarrow{k_{ISC}} {}^1\mathbf{CA}* \xrightarrow[\text{[D]}]{k_{ET}} \ ^1[\mathbf{D}^{•+}, \mathbf{CA}^{•−}] \qquad (3)$$
$$\text{singlet} \atop \text{radical-ion pair}$$

The direct observation of the excited singlet state of chloranil and its transformation to the triplet state has hitherto been hampered by instrumental limitations owing to its very short lifetime.[10] Thus, an initially broad absorption band was observed during the 30-ps laser excitation of chloranil in acetonitrile, which very rapidly evolved to the known spectrum of chloranil triplet.[11,12] The initial absorption was tentatively

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

(1) Patai, S. *The Chemistry of the Quinonoid Compounds*; Wiley: New York, 1974; Part 2.

(2) (a) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 15. (b) Dannenberg, H. *Synthesis* **1970**, 74.

(3) (a) Kawai, K.; Shirota, Y.; Tsubomura, H.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 77. (b) Maruyama, K.; Osuka, S. In ref 1. (c) Creed, D. In *Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds; CRC Press: Boca Raton, FL, 1995; p 737. (d) Bruce, J. M. *Chem. Soc. Quart. Rev.* **1967**, *21*, 405.

(4) (a) Baciocchi, E.; Del Giacco, T.; Elisei, F.; Ioele, M. *J. Org. Chem.* **1995**, *60*, 7974. (b) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317. (c) Lal, B.; Gidwani, R. M.; Reden, J.; de Souza, N. J. *Tetrahedron Lett.* **1984**, *25*, 2901.
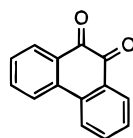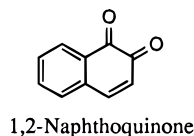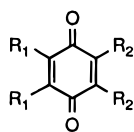
(5) Oikawa, Y.; Yashioka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1982**, 889.

(6) (a) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Dekker: New York, 1970. (b) Peover, M. E. *J. Chem. Soc.* **1962**, 4540.

(7) The reduction potential of the chloranil triplet ($E^*_{red}$) was calculated using the equation $E^*_{red} = E_T + E^0_{red}$, where $E_T$ is the triplet energy (2.13 eV)[8] and $E^0_{red}$ is the (ground-state) reduction potential (+0.02 V *vs* SCE)[6] of chloranil.

(8) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Dekker: New York, 1993.

(9) The energy of the first excited singlet state of chloranil is about 2.75 eV, as estimated from the low-energy cutoff of its absorption spectrum at 450 nm. Thus the singlet state of chloranil, with $E^*_{red} = 2.77$ V *vs* SCE, is expected to be a better oxidant than the triplet. (Compare footnote 7.)

(10) Hilinski, E. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 5193.

**Chart 1**

Chloranil: **CA**; $R_1 = R_2 = Cl$

Fluoranil: **FA**; $R_1 = R_2 = F$

Bromanil: **BA**; $R_1 = R_2 = Br$

Iodanil: **IA**; $R_1 = R_2 = I$

Duroquinone: **DQ**; $R_1 = R_2 = Me$

Dicyanodichloroquinone:
  **DDQ**; $R_1 = CN$; $R_2 = Cl$

1,2-Naphthoquinone

9,10-Phenanthrenequinone



**Figure 1.** Transient absorption spectra recorded (A) 1.5, (B) 4.0, (C) 9.0, and (D) 20 ps after photoexcitation of chloranil in dichloromethane with the 230-fs laser pulse at 400 nm. [All spectra are chirp-corrected; see text.]

assigned to the excited singlet state of chloranil, and an intersystem crossing rate constant of $k_{ISC} = 3 \times 10^{10}$ s$^{-1}$ was estimated.[10]  The recent extension of time-resolved laser techniques to the femtosecond time scale[13] now makes possible a systematic spectroscopic examination of this and other short-lived quinone singlet states and allows precise kinetic studies of their ultrafast reactions.

We wish to report femtosecond/picosecond pump-probe experiments[14] with chloranil and a series of other quinones (see Chart 1), which establish the electron-transfer reactivity of their singlet excited states. Complete absorption spectra of the excited singlet states and rate constants for both intersystem crossing to the triplet state and for electron-transfer quenching in the presence of electron donors are presented. Furthermore, the analysis of the ET quenching products leads to an unambiguous identification of the initially observed transients as the excited singlet states of the quinones.[15] Thus, on the basis of eq 2, the generation and identification of the singlet radical-ion pair, *e.g.*, $^1[D^{\bullet+}, CA^{\bullet-}]$, as a result of the electron-transfer quenching of the early excited state of the quinone, is put forward as conclusive evidence for the singlet character of the initial quinone transient. Finally, it is demonstrated that the efficiency of quinones as triplet sensitizers in electron-transfer reactions is not only based on very fast intersystem-crossing rates, but also on the rather long lifetimes of the resulting triplet radical-ion pairs as compared to those of the corresponding singlet ion pairs.[16]

## Results and Discussion

**1.  Direct Observation and Spectral Characterization of the Early Photoexcited States of Chloranil.**  A 5 mM solution of chloranil in dichloromethane was pale yellow in color due to a weak absorption band, centered at 376 nm, which extended into the visible wavelength range. Chloranil could thus be excited at 400 nm with a 230-fs laser pulse (2 mJ) generated by the amplified Ti:sapphire laser system. The design of the pump-probe spectrometer,[14] which employed a supercontinuum source for the probe light and a dual diode-array as detector, allowed us to record complete transient spectra in a single shot and to monitor simultaneously the spectral changes that occurred within the first 30 ps at various wavelengths. Owing to the rapidity of the spectral evolution (*vide infra*), it was necessary to correct for group velocity dispersion ("chirp").[17] Thus, the changes in absorbance over time were analyzed wavelength by wavelength, and for each wavelength-dependent kinetic trace, the time scale was shifted to position the zero-time point to correspond to 50% of the initial rise (see the Experimental Section). A series of chirp-corrected absorption spectra were then computer generated point-by-point by extracting the absorbance values from the time-corrected kinetic traces. The time-resolved spectra observed upon excitation of **CA** are shown in Figure 1. The spectrum at 1.5 ps after laser excitation shows a symmetrical absorption band with maximum at 505 nm. The rise time of this symmetrical absorption band was determined at various wavelengths and was found to be identical to the response time of the pump-probe experiment (700 fs) at all monitoring wavelengths.

Between 2 and 40 ps after laser excitation, the transient absorbance continued to increase, but at a slower rate. Moreover, the spectral band changed in shape, with the symmetrical spectrum at early times gradually developing fine structure. Thus, 30 ps after laser excitation, the original Gaussian band had evolved into a new band with a maximum at 510 nm, a shoulder at 480 nm, and a steep fall-off toward the longer wavelength range. This absorption band remained unchanged throughout the picosecond and nanosecond time scale, and was conclusively assigned to the $T_1 - T_n$ transition of triplet chloranil by comparison with the transient spectrum recorded previously.[11,12,18]

(11) Gschwind, R.; Haselbach, E. *Helv. Chim. Acta* **1979**, *62*, 941.

(12) (a) Kemp, D. R.; Porter, G. *J. Chem. Soc. D* **1969**, 1029. (b) Porter, G.; Topp, M. R. *Proc. R. Soc. London* **1970**, *A315*, 163. (c) Kobashi, H.; Gyoda, H.; Morita, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1731.

(13) (a) Manz, J.; Wöste, L. *Femtosecond Chemistry*; VCH: Weinheim, 1995. (b) Simon, J. D. *Rev. Sci. Instrum.* **1989**, *60*, 3597. (c) Martin, J.-L.; Migus, A.; Mourou, G. A.; Zewail, A. H. *Ultrafast Phenomena VIII*; Springer: New York, 1993.

(14) Hubig, S. M.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 3842.

(15) Besides the excited singlet state, other electronically and/or vibrationally excited states have been considered as precursors to the lowest excited triplet state ($T_1$). For an example of the $T_2$ state as precursor, see: (a) Hamanoue, K.; Nakayama, T.; Shiozaki, M.; Funasaki, Y.; Nakajima, K.; Teranishi, H. *J. Chem. Phys.* **1986**, *85*, 5698. (b) Hamanoue, K.; Nakayama, T.; Ito, M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3487. For vibrationally excited ("hot") triplet states as precursors, see: (c) Greene, B. I.; Hochstrasser, R. M.; Weisman, R. B. *J. Chem. Phys.* **1979**, *70*, 1247. (d) Wiederrecht, G. P.; Niemczyk, M. P.; Svec, W. A.; Wasielewski, M. R. *J . Am. Chem. Soc.* **1996**, *118*, 81. (e) Kliner, D. A. V.; Alfano, J. C.; Barbara, P. F. *J. Chem. Phys.* **1993**, *98*, 5375.

(16) Efficient photochemistry from the *singlet* excited states of quinones requires (i) ultrafast electron transfer from a donor to $^1$**CA**\* and (ii) fast follow-up reactions of the singlet radical-ion pairs to prevent the energy-wasting back-electron transfer to be discussed later. In contrast, electron-transfer quenching of quinone triplets leads to triplet radical-ion pairs which are long-lived owing to the spin restriction in the back-electron-transfer deactivation (see: Jones, G., II. In *Photoinduced Electron Transfer*, Part A; Fox, M. A., Chanon, M., Eds.; Elsevier: New York, 1988; p 245ff.
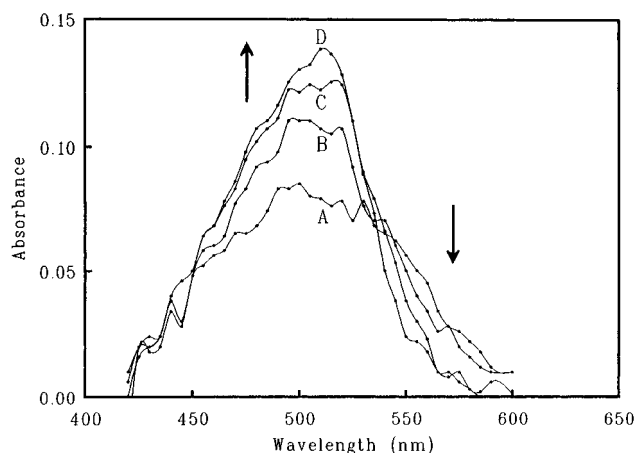
(17) (a) Sharma, D. K.; Yip, R. W.; Williams, D. F.; Sugamori, S. E.; Bradley, L. L. T. *Chem. Phys. Lett.* **1976**, *41*, 460. (b) Yip, R. W.; Korppi-Tommola, J. *Rev. Chem. Intermed.* **1985**, *6*, 33. For an example of the correction of a spectrum distorted by "chirp", see: (c) Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 3380.

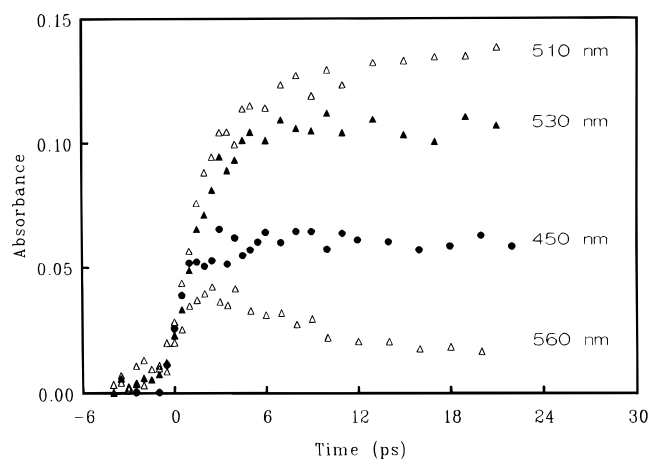(18) Jones, G., II; Haney, W. A. *J. Phys. Chem.* **1986**, *90*, 5410.

**Figure 2.** Kinetic traces extracted from the time-resolved transient spectra generated by 400-nm excitation of chloranil in dichloromethane.

**Chart 2.** Spectral Properties of the Photoexcited States of Chloranil.

|                              | $Q_1$*        | $Q_2$*          |
| ---------------------------- | ------------- | --------------- |
| $\lambda_{max}$ (nm)         | 505           | 510, 480 (sh)   |
| $\epsilon_{max}$ (M$^{-1}$ cm$^{-1}$) | 6,100 $\pm$ 300 | 7,600 $\pm$ 400 |
| Lifetime (ps)                | 8             | >10$^7$         |

In order to determine the extinction coefficient at the spectral maximum of the initial transient (spectrum A in Figure 1), we first determined the extinction coefficient of the triplet excited state of **CA** in dichloromethane by nanosecond laser photolysis. [Benzophenone was used as the actinometer and the triplet quantum yield was taken to be $\Phi_T = 1.0$, as described in the Experimental Section.] A quantitative comparison of the absorption spectra in Figure 1 allowed us then to determine the absorptivity of the early transient as $\epsilon_{505} = 6100 \pm 300$ M$^{-1}$ cm$^{-1}$.

Kinetic traces at four wavelengths in Figure 2 illustrate the gradual evolution of the initial symmetrical transient spectrum to the fine-structured unsymmetrical spectrum of **CA** triplet. These traces indicate biphasic kinetics, i.e., a fast growth of the initial absorption (within the time resolution of the pump-probe experiment), followed by a slower increase (at 510 nm), decay (at 560 nm), or no change (at 530 and 450 nm) of the absorbance signal to correlate with the spectral transformation described above. A first-order rate constant of 1.2 ($\pm$0.1) $\times$ 10$^{11}$ s$^{-1}$ was extracted from the analysis of the kinetic traces at 510 and 560 nm, which corresponded to the lifetime of 8 ps reported in Chart 2. The steady (unchanging) absorbances at 450 and 530 nm indicated isosbestic points at these wavelengths (compare Figures 1 and 2). Similar spectral changes and biphasic kinetics were observed in other solvents, and rate constants of $1.0 \times 10^{11}$, $8.4 \times 10^{10}$, and $6.1 \times 10^{10}$ s$^{-1}$ were obtained in acetonitrile, methanol, and benzene, respectively. In benzene solution, the formation of $^3$**CA**\* was accompanied by a concomitant growth of a weak, broad absorption extending beyond 800 nm. This new absorption band was assigned to the triplet exciplex, $^3$[**CA**, C$_6$H$_6$]\*, in accordance with previous reports.[19] However, the characteristic shape of the $^3$**CA** absorption band (with its maximum at 518 nm and shoulder at 490 nm) was not affected by this exciplex formation.

In summary, photoexcitation of chloranil (**CA**) generates two spectrally distinct transients, $Q_1$\* and $Q_2$\*, which are observed in rapid sequence on the early picosecond time scale (see

**Scheme 1**

$$\text{CA} \xrightarrow[\text{t} < 700\ \text{fs}]{h\nu} Q_1^* \xrightarrow[\text{t} \approx 10\ \text{ps}]{k_{obs}} Q_2^*$$
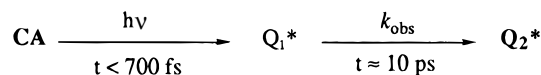
Scheme 1). The spectral changes associated with the conversion of $Q_1$\* to $Q_2$\* are characterized by three features that indicate a uniform transformation:[20] (i) At any chosen monitoring wavelength, the change (growth or decay) of the transient absorbance over time follows first-order kinetics. (ii) Exponential fits of the absorbance *vs* time diagrams yield a constant, wavelength-independent rate constant of $k_{obs} = 1.2 \times 10^{11}$ s$^{-1}$ for the transition from $Q_1$\* to $Q_2$\*. (iii) Two isosbestic points at 450 and 530 nm are observed in the time-resolved absorption spectra (see Figure 1). Such isosbestic points demonstrate the uniform transformation from $Q_1$\* to $Q_2$\* consistent with that presented in Scheme 1.[20] The spectral characteristics of the two transients $Q_1$\* and $Q_2$\* in dichloromethane are compared in Chart 2.

The absorption spectrum of the second transient ($Q_2$\*) is identical with the absorption spectrum of the chloranil triplet state (including the characteristic fine structure), as previously recorded on the microsecond time scale.[11,12,18] Thus, $Q_2$\* can be unambiguously assigned to the lowest triplet state (T$_1$) of chloranil ($^3$**CA**\*). On the other hand, there are several possible assignments for $Q_1$\*. For example, $Q_1$\* could be the first excited singlet state (S$_1$), which is known to be the precursor to the triplet state.[21] On the other hand, $Q_1$\* may be an electronically- or vibrationally-excited triplet species.[15] Since the spectral characteristics in Chart 2 cannot help in the assignment of the spin multiplicity of $Q_1$\*, we exploited multiplicity-specific electron-transfer processes, such as those described in eqs 1 and 2, to resolve this point. In particular, anisole (**AN**, methoxybenzene) was chosen as the electron donor to generate singlet and triplet radical-ion pairs in two ways. First, the *singlet* ion pair, $^1$[**AN**$^{\bullet+}$, **CA**$^{\bullet-}$], was unambiguously generated by charge-transfer excitation of the electron donor–acceptor (EDA) complex formed by chloranil at high concentrations of anisole. Second, the *triplet* ion pair, $^3$[**AN**$^{\bullet+}$, **CA**$^{\bullet-}$], was generated by the diffusional quenching of triplet chloranil at low concentrations of anisole, as described below.

**2. Assignment of the Early Chloranil Transient to the Singlet State Based on Its Electron-Transfer Behavior. (a) Electron Transfer from Anisole.** First, we irradiated a 1.2 mM solution of chloranil in neat anisole. This approach ensured that every chloranil molecule was in van der Waals contact with the aromatic donor, and that the rate of electron transfer between chloranil and anisole would not be limited by diffusion.[22] Moreover, chloranil forms electron donor–acceptor (EDA) complexes with anisole.[23a] Since the charge-transfer absorption band of the EDA complex strongly overlaps with the local absorption of **CA**, laser irradiation at $\lambda_{exc}$ = 400 nm excited mainly the charge-transfer transition of the EDA complex.[23b] As shown in Figure 3, a transient absorption centered at 450 nm developed during the period of the laser excitation, and it subsequently decayed to the spectral baseline within 10 ps. The decay rate was determined by an exponential fit of the kinetic

(19) Tahara, T.; Hamaguchi, H-O. *J. Phys. Chem.* **1992**, *96*, 8252.

(20) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; p 49.

(21) Absorptions leading to *direct* population of the triplet state from the (singlet) ground state have been observed in some cases. However, these spin-forbidden S$_0$–T$_1$ absorptions are extremely weak ($\epsilon \approx 10^{-5}$ M$^{-1}$ cm$^{-1}$). See: Wayne, R. P. *Principles and Applications of Photochemistry*; Oxford University Press: Oxford, 1988; p 83.

(22) Diffusion-controlled reactions occur with bimolecular rate constants of about 10$^{10}$ M$^{-1}$ s$^{-1}$. See ref 20, p 239.

(23) (a) Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: New York, 1969; p 40. (b) In this solution, the relative absorbance of [**AN, CA**] and **CA** at $\lambda_{exc}$ = 400 nm was >15.

*Identification of Photoexcited Singlet Quinones*

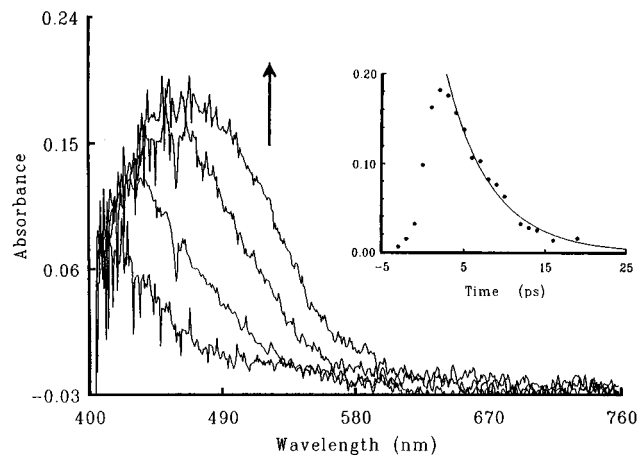*J. Am. Chem. Soc., Vol. 119, No. 12, 1997* 2929



**Figure 3.** Transient absorption spectra showing the rise of the chloranil radical anion from $-1.0$ to 2.0 ps following the 400-nm laser excitation of chloranil in neat anisole. [The spectra are uncorrected to demonstrate the spectral "chirp".] The inset shows the rise and decay of the absorption band (monitored at 450 nm) and the monoexponential simulation of the decay kinetics (solid line).

traces (monitored at 450 nm) to first-order kinetics (see inset in Figure 3), and a rate constant of $1.9\ (\pm0.1) \times 10^{11}$ s$^{-1}$ was extracted. Neither the initial transient of chloranil Q$_1$* (observed in the absence of electron donors) nor **CA** triplet (with its characteristic absorption spectrum) was observed. The 450-nm transient was readily assigned to combined absorptions of anisole cation radical (**AN**$^{\bullet+}$) and chloranil anion radical (**CA**$^{\bullet-}$) based on the comparison with the authentic spectra reported in the literature.[24,25]

According to Mulliken theory,[26] photoexcitation of the charge-transfer or CT absorption band of an EDA complex induces a one-electron transfer from the donor to the acceptor to generate the ion pair.[27] Thus, laser excitation of the chloranil/anisole complex leads to instantaneous[28] formation of the radical-ion pair consisting of anisole cation radical (**AN**$^{\bullet+}$) and chloranil anion radical (**CA**$^{\bullet-}$), *i.e.* [**AN**$^{\bullet+}$, **CA**$^{\bullet-}$]. Chloranil anion radical exhibits an absorption maximum at 450 nm with an extinction coefficient of $\epsilon_{max} = 9600$ M$^{-1}$ cm$^{-1}$,[25] and anisole cation radical shows an absorption centered at $\lambda_{max} = 435$ nm and $\epsilon_{max} = 4400$ M$^{-1}$ cm$^{-1}$.[24] The absorption spectrum in Figure 3 thus represents the composite absorption of **AN**$^{\bullet+}$ and **CA**$^{\bullet-}$. Since the prompt electron transfer to form the radical pair occurs much faster than spin inversion, the product radical-ion pair remains in the same spin state as the reactants from which it is generated.[29] In other words, the EDA complex of **CA** and **AN** (both in their singlet ground states) is directly

(24) Kim, E. K.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1993**, *115*, 3091.

(25) André, J. J.; Weill, G. *Mol. Phys.* **1968**, *15*, 97.

(26) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600. (b) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (c) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(27) Mulliken theory has been verified by picosecond time-resolved spectroscopy. See: (a) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147. Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 5834. (b) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068. (c) Ebbesen, T. W.; Manring, L. E.; Peters, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 7400. (d) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071. (e) Wynne, K.; Galli, C.; Hochstrasser, R. M. *J. Chem. Phys.* **1994**, *100*, 4797. (f) Hubig, S. M. *J. Phys. Chem.* **1992**, *96*, 2903. See also ref 15.

(28) Time-resolved spectroscopy by Mataga,[27a] Hochstrasser,[27e] and co-workers has established that charge-transfer excitation effects the transfer of an electron from the donor to the acceptor within 500 fs.

(29) (a) The formation of singlet radical-ion pairs upon electron-transfer quenching of an excited singlet state has been established earlier.[29b,c,30b,41] (b) Weller, A. *Z. Phys. Chem. N. F.* **1982**, *130*, 129. (c) Weller, A. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1976; p 23.
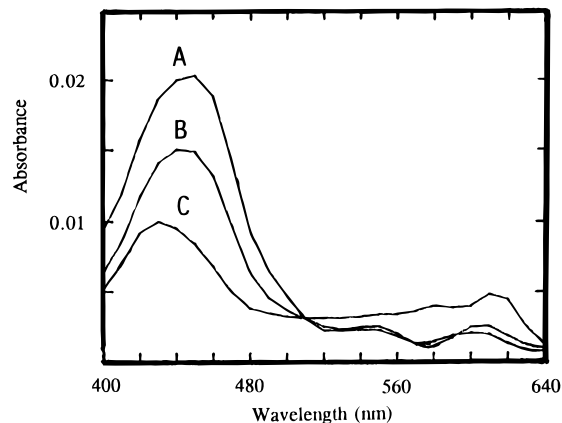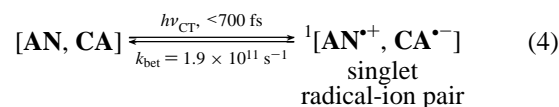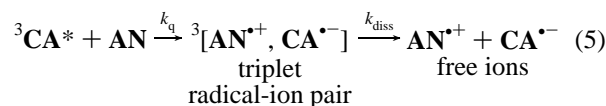


**Figure 4.** Transient spectra obtained (A) 0.8, (B) 1.6, (C) 7.0 $\mu$s after 10-ns laser excitation of chloranil (2.5 mM) in the presence of 0.012 M anisole in dichloromethane.

excited to the spin-correlated *singlet* radical-ion pair, *i.e.*

$$[\mathbf{AN, CA}] \underset{k_{bet} = 1.9 \times 10^{11}\ s^{-1}}{\overset{h\nu_{CT},\ <700\ fs}{\rightleftharpoons}} {}^1[\mathbf{AN^{\bullet+}, CA^{\bullet-}}] \quad (4)$$
$$\text{singlet radical-ion pair}$$

This radical-ion pair rapidly reverts to the ground-state EDA complex within 10 ps of laser excitation, to indicate that the return electron transfer ($k_{bet}$) is unencumbered by spin-dynamical processes.

Electron-transfer quenching of *triplet* chloranil ($^3$**CA**) by anisole at low concentrations (0.012 M) in dichloromethane generated transient absorption spectra that were identical with those obtained by charge-transfer excitation on the early picosecond time scale, but the ions **AN**$^{\bullet+}$ and **CA**$^{\bullet-}$ persisted for more than 10 $\mu$s as shown in Figure 4. Quenching of $^3$**CA**$^*$ by electron transfer from anisole generates the *triplet* radical-ion pair to accord with the conservation of spin. For the triplet ion pair, return electron transfer to ground-state (singlet) reactants is spin-forbidden, and thus expected to be rather slow. Indeed, the extended lifetime of this ion pair permits dissociation to the free ions, *i.e.*

$$^3\mathbf{CA}^* + \mathbf{AN} \overset{k_q}{\longrightarrow} {}^3[\mathbf{AN^{\bullet+}, CA^{\bullet-}}] \overset{k_{diss}}{\longrightarrow} \mathbf{AN^{\bullet+}} + \mathbf{CA^{\bullet-}} \quad (5)$$
$$\text{triplet radical-ion pair} \qquad \text{free ions}$$

[Note that the process of dissociation ($k_{diss}$) takes place on the diffusional time scale of *circa* $10^{-9}$ s.][30] The ultimate fate of the free ions is bimolecular recombination that follows second-order kinetics on the microsecond time scale.

In summary, the spectacular difference in lifetime for singlet and triplet radical-ion pairs over three orders of magnitude forms the basis for distinguishing them even though they are spectrally indistinguishable. Thus, singlet radical-ion pairs collapse on the early picosecond time scale, whereas triplet radical-ion pairs persist on the nanosecond time scale. These results imply the general rule that electron-transfer quenching of excited singlet states generates short-lived ion pairs, whereas quenching of triplet states yields long-lived ion pairs. This rule can now be exploited to determine the spin multiplicity of Q$_1$* as follows: The Q$_1$* state of chloranil can be quenched by high concentrations of an electron donor prior to triplet formation, and the lifetime of the resulting ion pair relates to its spin multiplicity. The spin multiplicity of the ion pair, in turn, will reveal the spin state of Q$_1$*. For this experiment, we chose hexaethyl-

(30) (a) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1396. (b) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges.* **1968**, *72*, 257.

benzene (**HEB**) as electron-transfer quencher for the following reasons: **HEB** is a good electron donor ($E^o = 1.59$ V *vs* SCE),[31] which—unlike anisole—does not form EDA complexes with chloranil even at concentrations close to saturation (1.8 M).[32] **HEB** can thus be employed in very high concentrations to quench the early photoexcited state of chloranil ($Q_1^*$) without complications resulting from the interference of the charge-transfer excitation of an [**HEB, CA**] complex.

**(b) Electron Transfer from Hexaethylbenzene.** A solution of 5 mM **CA** and 1.8 M **HEB** in dichloromethane was irradiated with the 230-fs Ti:sapphire laser pulse at 400 nm (1.8 mJ). At early times, the growth of transient absorptions was observed over a wavelength range from 400 to 600 nm with a maximum at 450 nm. This initial absorption evolved in a complex fashion over the subsequent monitoring period from 0 to 200 ps. We ascribe these complex series of transient spectra to the composite absorptions of the first transient ($Q_1^*$), triplet chloranil ($^3$**CA**$^*$), chloranil anion radical (**CA**$^{•-}$), and hexaethylbenzene cation radical (**HEB**$^{•+}$). To describe the changes associated with the severely overlapping bands, we analyzed the kinetics at various wavelengths as follows: At 560 nm, the absorption decayed within 10 ps (see Figure 5A) with a rate constant of $1.8 \times 10^{11}$ s$^{-1}$. At 510 and 450 nm (see Figure 5, parts B and C, respectively), only a partial decrease in the absorption was monitored on the same time scale. The resulting residual absorption did not change significantly over the subsequent 30 ps. First-order rate constants for the partial decays were determined from the exponential fit of the absorbance data to a raised baseline and $k_{510} = 2.4 \times 10^{11}$ s$^{-1}$ and $k_{450} = 1.9 \times 10^{11}$ s$^{-1}$ were obtained for the monitoring wavelengths 510 and 450 nm, respectively. The spectral kinetics are summarized in Table 1, and they are compared to those obtained in the absence of **HEB** (*vide supra*).

The residual absorbances on the early picosecond time scale continued to change, but at a much slower rate. A narrow band at 450 nm developed within hundreds of picoseconds, and the absorption at wavelengths greater than 500 nm decayed at the same rate (see Figure 6). The spectrum obtained after 250 ps exhibited a strong narrow peak at 450 nm and a broad shoulder around 500 nm, which matched closely the transient spectrum obtained 1 $\mu$s after 355-nm excitation of a mixture of **CA** and **HEB** with a 10-ns Nd:YAG laser pulse (see the inset to Figure 6). The 450-nm transient was easily assigned to the **CA**$^{•-}$ anion radical[25] (*vide supra*), and the 500-nm shoulder in Figure 6 was ascribed to the absorption of the cation radical **HEB**$^{•+}$. [The authentic spectrum of **HEB**$^{•+}$ was obtained in an independent picosecond-laser experiment by charge-transfer excitation (355 nm) of the electron donor−acceptor complex of **HEB** with maleic anhydride in dichloromethane.]

If the concentration of **HEB** was adjusted to 1.0 M, the overall pattern of the spectral transformations was found to be the same as those obtained with 1.8 M **HEB**. However, the extent of the early-picosecond decay, monitored at 560, 510, and 450 nm, was less pronounced as compared to the kinetic traces shown in Figure 5, and the rate constant of the slow transformation (100−500 ps) in Figure 6 was determined to be $(9 \pm 1) \times 10^9$ s$^{-1}$.

These laser experiments with chloranil in the presence of **HEB** were analyzed as follows: Upon laser excitation, the early

(31) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(32) The conformational structure of hexaethylbenzene with the methyl groups projecting alternately above and below the ring plane (see: Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc* . **1981**, *103*, 6073) precludes the close approach of a quinone $\pi$-acceptor, as required in the formation of intermolecular EDA complexes. The full implications of such steric hindrance on CT complex formation will be reported in a forthcoming paper (Rathore, R. Unpublished results).
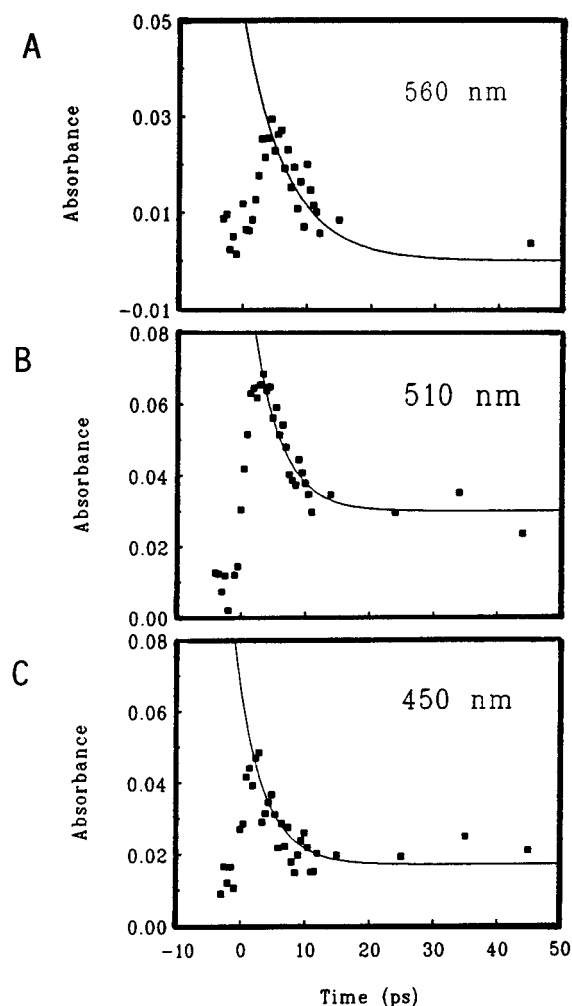


**Figure 5.** Time dependence of the transient absorbances, monitored at various wavelengths, upon 400-nm excitation of chloranil in dichloromethane in the presence of hexaethylbenzene (**HEB**, 1.8 M). The solid lines represent the best fits of the data points to first-order kinetics.

**Table 1.** Kinetics of the Chloranil Transients in the Presence and Absence of Hexaethylbenzene[a]

| [**HEB**] | monitoring wavelengths (nm) | | |
| (M) | 450 | 510 | 560 |
| --- | --- | --- | --- |
| 0 | (isosbestic point) | $k_g = 1.2 \times 10^{11}$ s$^{-1}$ | $k_d = 1.2 \times 10^{11}$ s$^{-1}$ |
| 1.8 | $k_d = 1.9 \times 10^{11}$ s$^{-1}$ | $k_d = 2.4 \times 10^{11}$ s$^{-1}$ | $k_d = 1.8 \times 10^{11}$ s$^{-1}$ |

[a] The rate constants $k_d$ and $k_g$ represent the first-order spectral decay and growth, respectively.
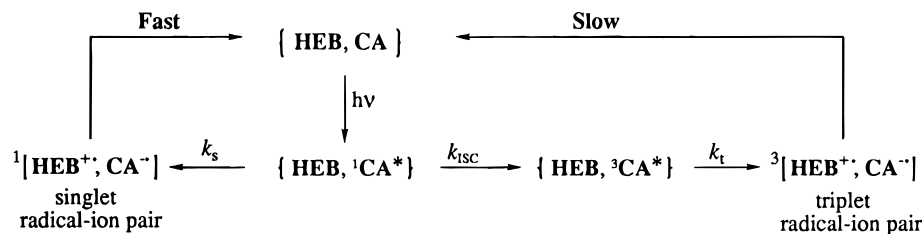
spectra with an absorption maximum at 450 nm represent the superposition of the spectra of chloranil anion radical (**CA**$^{•-}$)[25] and $Q_1^*$. [The absorption band of the latter species is centered at 505 nm and tails beyond 580 nm, see Figure 1.] The instantaneous formation of **CA**$^{•-}$ is not the result of charge-transfer excitation since **HEB** does not form EDA complexes with chloranil.[32] However, it can be explained as the result of static quenching of $Q_1^*$ by **HEB** as follows: A 1.8 M solution of **HEB** in dichloromethane implies a molar ratio of 0.12 between solute and solvent molecules. Thus, on average, every eighth molecule in the first solvation shell of an excited **CA** molecule is an **HEB** donor. Consequently, efficient electron-transfer quenching of $Q_1^*$ occurs and the resulting ion pair [**HEB**$^{•+}$, **CA**$^{•-}$] is detected within the first few picoseconds following laser excitation.[33] Since diffusional encounters—even at concentrations as high as 1.8 M—require more than 50 ps to

(33) The weak absorbance of **HEB**$^{•+}$, with $\lambda_{max} = 500$ nm, is masked by the strong absorbance of $Q_1^*$.

**Scheme 2**



(The braces { } indicate that chloranil and **HEB** are in van der Waals contact.)

take place,[34] we conclude that $Q_1^*$ is *statically* quenched by **HEB** molecules that are already in van der Waals contact with the (excited) chloranil. Consequently, we will exploit static quenching to obtain ultrafast electron-transfer rate constants that cannot otherwise be evaluated by the standard Stern–Volmer methodology.

The transient spectra undergo significant changes on the early picosecond time scale, as illustrated for various monitoring wavelengths in Figure 5. First, we analyze the kinetic trace at 560 nm where only the initial transient $Q_1^*$ absorbs, and $^3CA^*$, $CA^{\bullet-}$, and $HEB^{\bullet+}$ exhibit negligible absorption (compare Figures 1 and 6). The decay of $Q_1^*$, monitored at this wavelength (with $k_d = 1.8 \times 10^{11}$ s$^{-1}$), is 1.5 times faster in the presence of 1.8 M **HEB** than in its absence ($k_d = 1.2 \times 10^{11}$ s$^{-1}$, see Table 1). This increase in the decay rate is ascribed to electron-transfer quenching of the $Q_1^*$ state by **HEB** leading to the radical-ion pair, [**HEB**$^{\bullet+}$, **CA**$^{\bullet-}$]. Figure 5C shows the kinetic behavior monitored at 450 nm, where the predominantly absorbing species is $CA^{\bullet-}$ ($\epsilon_{450} = 9600$ M$^{-1}$ cm$^{-1}$),[25] and where $Q_1^*$ and $^3CA^*$ do not contribute significantly to the overall transient absorbance ($\epsilon_{450} \approx 2000$ M$^{-1}$ cm$^{-1}$ for both species, see Figure 1). Thus, the decay monitored at 450 nm in Figure 5C with $k_d = 1.9 \times 10^{11}$ s$^{-1}$ is predominantly due to back-electron transfer from $CA^{\bullet-}$ to $HEB^{\bullet+}$ within the initially formed radical-ion pair. This fast rate is indicative of back-electron transfer within a *singlet* ion pair $^1$[**HEB**$^{\bullet+}$, **CA**$^{\bullet-}$] (compare the decay rate in the case of chloranil in anisole, *vide supra*), and its formation due to the quenching of $Q_1^*$ implies that the quenched species is indeed the excited *singlet* state of chloranil, *i.e.*, $Q_1^* = {}^1CA^*$.

At 510 nm, we simultaneously monitor a mixture of all transients, *i.e.* $Q_1^*$, $^3CA^*$, $CA^{\bullet-}$, and $HEB^{+\bullet}$, which hampers a quantitative analysis of the kinetic trace in Figure 5B. However, the partial decay with a rate constant of $2.4 \times 10^{11}$ s$^{-1}$ is

predominantly caused by back-electron transfer from $CA^{\bullet-}$ to $HEB^{\bullet+}$ within the singlet ion pair. The residual absorbance remaining beyond 10 ps is ascribed to the triplet state of chloranil which derives from the unquenched singlet.[34c] This assignment is based on the following observations and conclusions: The residual 510-nm absorption in Figure 5B decays, and the residual 450-nm absorption (of Figure 5C) increases between 50 and 250 ps with the same rates (see Figure 6), ultimately leading to the spectrum shown in the inset to Figure 6 (which remains unchanged over several nanoseconds). The spectral changes within 250 ps are ascribed to electron-transfer quenching of *triplet* chloranil by **HEB** to generate a triplet radical-ion pair, $^3$[**HEB**$^{\bullet+}$, **CA**$^{\bullet-}$].[34] Thus, two distinct ion pairs—singlet and triplet, with distinct lifetimes of 5 ps and several nanoseconds, respectively—are formed by electron-transfer quenching of singlet and triplet chloranil, as summarized in Scheme 2.

In summary, the photoinduced electron-transfer experiments with **HEB** lead to the following conclusions: (i) Photoexcitation of **CA** in the presence of **HEB** generates two distinct ion pairs with widely varying lifetimes. (ii) The short-lived ion pair, with a lifetime of less than 5 ps, is generated by electron-transfer quenching of the excited singlet state of chloranil ($^1CA^*$) by **HEB** ($k_s$ in Scheme 2), and it is the singlet ion pair. (iii) Singlet chloranil that escapes the electron-transfer quenching undergoes intersystem crossing to the excited triplet ($k_{ISC}$). Electron transfer to this species ($k_t$) generates the triplet ion pair. Since back-electron transfer from this ion pair is spin-forbidden, it persists for long times (nanoseconds) following the excitation.

**3. Identification and Spectral Characterization of the Photoexcited States of Other Quinones.** The series of the other quinones in Chart 1 including tetrasubstituted 1,4-benzoquinones,[35] 1,2-naphthoquinone, and 9,10-phenanthrene-quinone were also investigated in dichloromethane and in acetonitrile with the femtosecond laser system. The transient absorption spectra of the halogen-substituted benzoquinones, fluoranil (**FA**), bromanil (**BA**), and iodanil (**IA**) changed significantly with time in a manner similar to that observed with chloranil. Thus, the early spectra (at times between 1 and 5 ps) consisted of symmetrical absorption bands, but spectra with more fine structure were observed at later times (>20 ps). In all cases, the later absorption spectra were identified as those of the triplet states since they were identical to the transient spectra obtained on the microsecond time scale.[36] For example,
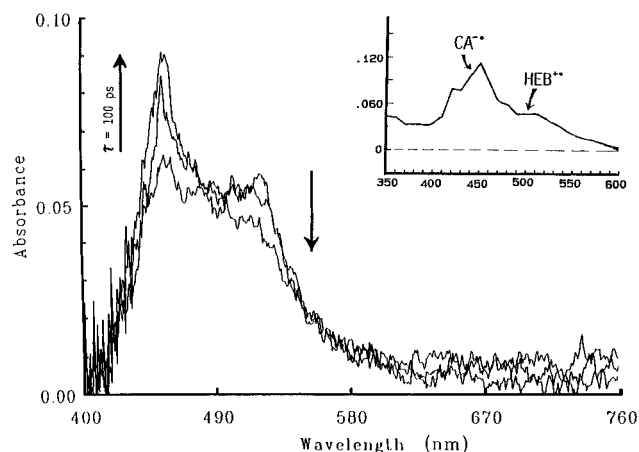


**Figure 6.** Transient absorption spectra recorded 50 to 250 ps following the 355-nm (30 ps) excitation of chloranil in dichloromethane in the presence of 1.0 M hexaethylbenzene. The inset shows the transient spectrum recorded 1.0 μs after excitation of the same solution.

(34) (a) The bimolecular rate constant for electron-transfer quenching of triplet chloranil by **HEB** was determined to be $k_q = 8.0 \times 10^9$ M$^{-1}$ s$^{-1}$.[34b] Even at concentrations of 1.0 M, the observed first-order quenching rate constant of 9 ($\pm$1) $\times$ 10$^9$ s$^{-1}$ is consistent with this bimolecular, diffusion-controlled[22] rate constant. In solutions saturated with **HEB** (*ca.* 1.8 M), diffusional quenching occurs with a pseudo-first-order rate of $k_{obs} = k_q[\mathbf{HEB}] \approx 2 \times 10^{10}$ s$^{-1}$. Thus diffusional encounters with $^3CA^*$ take place on a time scale of $k_{obs}^{-1} = 50$ ps. (b) Hubig, S. M. Unpublished results. (c) As useful as **HEB** has been, we continue to search for an even more effective donor to circumvent this complication.

(35) The unsubstituted quinone (1,4-benzoquinone) yielded only very weak transient absorption signals upon femtosecond-laser excitation.
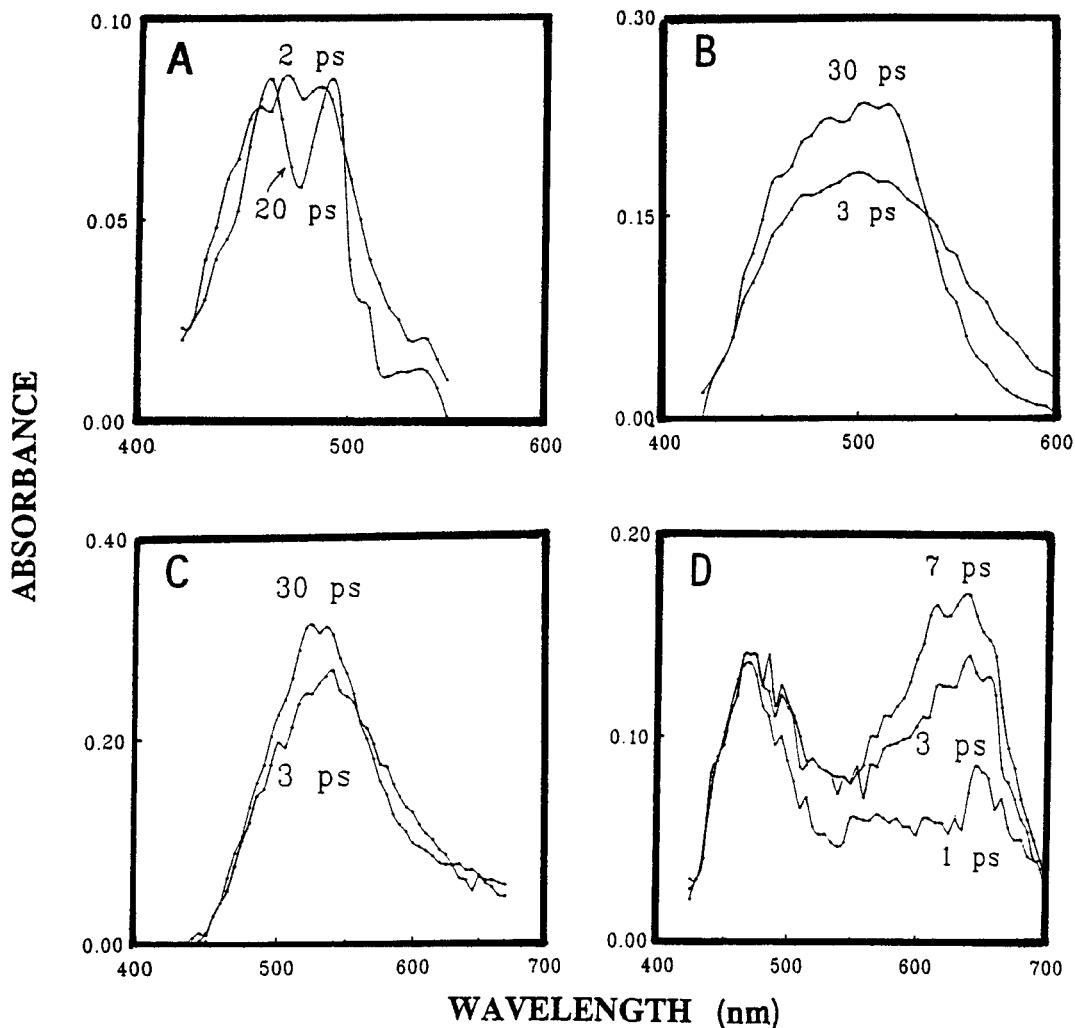
**Figure 7.** Transient absorption spectra recorded at the indicated times following the 400-nm laser excitation of (A) fluoranil, (B) bromanil, (C) iodanil, and (D) dicyanodichlorobenzoquinone (**DDQ**) in dichloromethane. All spectra are chirp-corrected.

the transient spectrum of **FA** (see Figure 7A) consisted of one symmetrical broad band with an absorption maximum at 470 nm at early times, which evolved into a characteristic double band with two equally intense maxima at 460 and 495 nm.[36] The bromanil transient spectrum (see Figure 7B) featured first one broad band centered at 500 nm, which then developed over 32 ps into the triplet spectrum. [The narrow tip at 515 nm and a steep fall-off at the red edge of the absorption band were reminiscent of the spectrum of $^3$**CA**\*.] The iodanil spectra (see Figure 7C) showed initially a maximum at 540 nm which later (after 50 ps) shifted slightly to 530 nm. Again, a steep fall-off on the red edge was observed.

The time-resolved spectra of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (**DDQ**) in dichloromethane were unique in the series of tetrasubstituted benzoquinones, in that they exhibited two absorption bands, one centered at 470 nm and the other centered at 640 nm (see Figure 7D). The chirp-corrected spectra show that initially (at 1 ps delay) only the 470-nm absorption band appears, whereas at later times (7 ps) after laser excitation the spectrum consists of both the 470- and the 640-nm band. The latter transient spectrum was ascribed to the triplet state of **DDQ** by comparison with the identical spectrum observed after 4 ns (and on the microsecond time scale). Thus, the rate constant for the spectral change was determined by monitoring the growth of the 640-nm band over time, and a rate constant of $2.5 \times 10^{11}$ s$^{-1}$ was extracted. In the case of the tetramethyl-substituted duroquinone (**DQ**), there was no *initially-formed*

transient within the rise time of the laser system. Instead, a transient absorption grew in over a period of 20 ps in both dichloromethane and acetonitrile solution (see Figure 8), which was identical to the spectrum of the **DQ** triplet.[37] The kinetics of this growth (monitored at 486 nm) did not exhibit the biphasic pattern characteristic of chloranil and the other tetrahaloquinones (compare Figure 2), and the steady growth of the spectral band over 20 ps was satisfactorily simulated as a simple monoexponential rise (see inset to Figure 8).

As examples of *o*-quinones, 1,2-naphthoquinone and 9,10-phenanthrenequinone were included in this study.[38] The spectral changes observed upon excitation of 1,2-naphthoquinone in dichloromethane are shown in Figure 9A. At early times, a broad absorption band with a maximum at 500 nm was detected which strongly shifted with time toward the longer wavelength range, ultimately yielding a very broad absorption band, centered at 600 nm and extending from below 460 nm to above 760 nm with a strongly structured shape. The spectrum recorded after 30 ps was identical to that assigned previously to the triplet state of 1,2-naphthoquinone.[39] Very different was the spectral evolution of 9,10-phenanthrenequinone in dichloromethane solution, for which the formation of the triplet[39] was marked

(36) Darmayan, A. P.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 6317.

(37) (a) Levin, P. P.; Tatikolov, A. S.; Kuzmin, V. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1982**, *31*, 890. (b) Levin, P. P.; Pluzhnikov, P. F.; Kuzmin, V. A. *Chem. Phys. Lett.* **1988**, *147*, 283. (c) Scaiano, J. C.; Neta, P. *J. Am. Chem. Soc.* **1980**, *102*, 1608. (d) Nagaoka, S.-I.; Ishihara, K. *J. Am. Chem. Soc.* **1996**, *118*, 7361.

(38) Photoexcitation of *o*-chloranil in dichloromethane did not yield any transients in the spectral range from 350 to 750 nm.

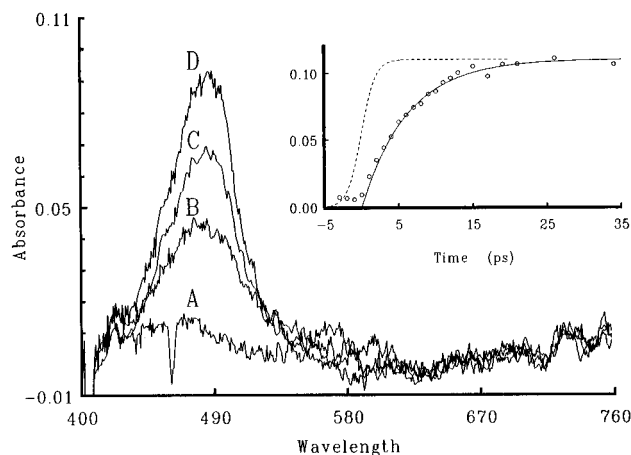(39) Becker, R. S.; Natarajan, L. V. *J. Phys. Chem.* **1993**, *97*, 344.

**Figure 8.** Transient spectra recorded (A) 0.0, (B) 3.0, (C) 6.0, and (D) 11 ps after 400-nm laser excitation of duroquinone in dichloromethane. [The spectra are not corrected for spectral chirp.] The inset shows the kinetic trace monitored at the absorption maximum of 486 nm. The solid line shows the best fit of the data points to a monoexponential rise, and the dotted line represents the response profile of the laser spectrometer.

by only a very subtle blue-shift from 485 to 480 nm in the absorption maximum (see Figure 9B). The rate constants for intersystem crossing obtained from the spectral dynamics on the early picosecond time scale, determined for this series of quinones in various solvents, are compiled in Table 2.

Femtosecond laser photolysis of a solution containing 2.5 mM bromanil and 1.8 M hexaethylbenzene in dichloromethane resulted in a series of spectral changes and kinetic decay patterns that were similar to those discussed in detail for the **CA/HEB** system (*vide supra*). For example, the fast decay of the absorbance signal to the baseline was monitored at 560 nm, whereas at 510 and 450 nm, partial decays to raised baselines were detected on the same time scale. The residual spectrum consisted of a composite of the absorption bands of the bromanil anion radical and hexaethylbenzene cation radical. [An authentic sample of bromanil anion radical was generated in a separate nanosecond-laser experiment by quenching of excited bromanil (1.5 mM) with biphenyl (5.4 mM) in acetonitrile solution.] As with chloranil, the ultrashort lifetime of $\mathbf{BA^{\bullet-}}$ was indicative of the singlet character of the $[\mathbf{HEB^{\bullet+}}, \mathbf{BA^{\bullet-}}]$ radical-ion pair. The formation of the singlet radical-ion pair, in turn, indicated that the quenched transient was indeed the singlet excited bromanil ($^1\mathbf{BA^*}$, *vide supra*).

On the basis of the results with chloranil and bromanil, we draw the general conclusion that in all cases in this study the early transient $Q_1^*$ observed upon photoexcitation of quinone is the excited singlet state. Consequently, the spectral changes monitored on the early picosecond time scale in the *absence* of electron donors are ascribed to intersystem crossing to the triplet manifold, whereas in the *presence* of effective donors such as anisole or **HEB** the singlet excited states are rapidly quenched by electron transfer as described in eq 2.

**4. The Generalized Dynamics of the Excited States of Quinones in Photosensitized Reactions. (a) Electron Transfer to Triplet and Singlet Excited Quinones.** The rapid intersystem-crossing rates for the quinones implies efficient formation of their reactive triplets. As a result, the ability of quinones to sensitize photoreactions on the triplet manifold is comparable to that of classical triplet sensitizers, such as benzophenone.[40] Indeed, the measured rate constants for

**Table 2.** Solvent Dependence for the Rate Constants for Intersystem Crossing ($k_{ISC}$) of Quinone Sensitizers

| | $k_{ISC}$ ($10^{11}$ s$^{-1}$) | |
| --- | --- | --- |
| quinone | CH$_3$CN | CH$_2$Cl$_2$ |
| 1,4-benzoquinone | *a* | *a* |
| fluoranil | 0.9 | 0.87 |
| chloranil | 1.0 | 1.2 |
| bromanil | 0.60 | 0.92 |
| iodanil | *b* | 1.2 |
| duroquinone | 2.0 | 1.8 |
| DDQ[c] | 1.6 | 2.5 |
| 1,2-naphthoquinone | *b* | 1.2 |
| 9,10-phenanthrenequinone | *b* | 0.56 |

[a] Not measured owing to weak transient absorption signals. [b] Not measured. [c] 2,3-Dicyano-5,6-dichloro-1,4-benzoquinone.

intersystem crossing ($k_{ISC} = 0.6$ to $2.5 \times 10^{11}$ s$^{-1}$) for the quinones in Table 2 match those reported recently for benzophenone ($k_{ISC} \approx 1 \times 10^{11}$ s$^{-1}$).[41,42] Thus, it is not surprising that quinones, especially chloranil, are extensively used in photochemical applications. However, chloranil follows a pattern of reactivity that is different from that of typical triplet sensitizers. For example, benzophenone is most commonly utilized as *energy-transfer* reagent due to its rather poor oxidizing properties ($E^0_{red} = -1.68$ V *vs* SCE).[43] Chloranil, on the other hand, is mostly employed in photosensitized *electron-transfer* processes owing to its high reduction potential.[7] In accord with this distinction, single electron transfers from donors (D) such as aromatic hydrocarbons,[4] alkenes,[4] amines,[4] and enol ethers[44] to $^3\mathbf{CA^*}$, *i.e.*,

$$^3\mathbf{CA^*} + \mathbf{D} \xrightarrow{k_t} {}^3[\mathbf{D^{\bullet+}, CA^{\bullet-}}] \xrightarrow[\text{slow}]{k_{bet}} \mathbf{CA} + \mathbf{D} \qquad (6)$$

are the basis for the rich photochemistry of chloranil, which in some cases has been directly monitored by time-resolved spectroscopy.[10,11,18,44] The triplet radical-ion pair is the crucial intermediate which can undergo further transformation to the photoproducts since the energy-wasting reversion to the starting materials ($k_{bet}$) is spin-forbidden and thus rather slow.

The excited singlet state ($^1\mathbf{CA^*}$), which is the direct precursor to the triplet, also acts as a one-electron oxidant in its own right, *i.e.*,

$$^1\mathbf{CA^*} + \mathbf{D} \xrightarrow{k_s} {}^1[\mathbf{D^{\bullet+}, CA^{\bullet-}}] \xrightarrow[\text{fast}]{k_{bet}} \mathbf{CA} + \mathbf{D} \qquad (7)$$

To compare the quenching rate constants of singlet and triplet chloranil (*i.e.* $k_s$ and $k_t$ in eqs 7 and 6, respectively), let us evaluate the different nature of the two quenching processes. In the case of the quenching of singlet chloranil in eq 7, "static" (*vide supra*) electron transfer occurs within the response time of the pump-probe experiment, and the observed first-order rate constant $k_s$ must exceed $10^{11}$ s$^{-1}$. On the other hand, electron transfer to triplet chloranil in eq 6 is diffusion-limited, as indicated by the measured value of the rate constant for bimolecular quenching of $k_t = 9 \times 10^9$ M$^{-1}$ s$^{-1}$. We conclude that electron transfer within the encounter complex, $\{^3\mathbf{CA}, \mathbf{HEB}\}$ in Scheme 2, is much faster than its formation by diffusion. Indeed, since the quenching of $^3\mathbf{CA^*}$ remains

(40) (a) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem. Photobiol.* **1985**, *30*, 81. (b) Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5074.

(41) Miyasaka, H.; Morita, K.; Kamada, K.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3385.

(42) (a) Tamai, N.; Asahi, T.; Masuhara, H. *Chem. Phys. Lett.* **1992**, *198*, 413. (b) Ikeda, N.; Imagi, K.; Masuhara, H.; Nakashima, N.; Yoshihara, K. *Chem. Phys. Lett.* **1987**, *140*, 281. (c) McGarry, P. F.; Doubleday, C. E.; Wu, C.-H.; Staab, H. A.; Turro, N. J. *J. Photochem. Photobiol. A: Chem.* **1994**, *77*, 109.

(43) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1974**, *96*, 6270.

(44) Bockman, T. M.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1623, 1633.
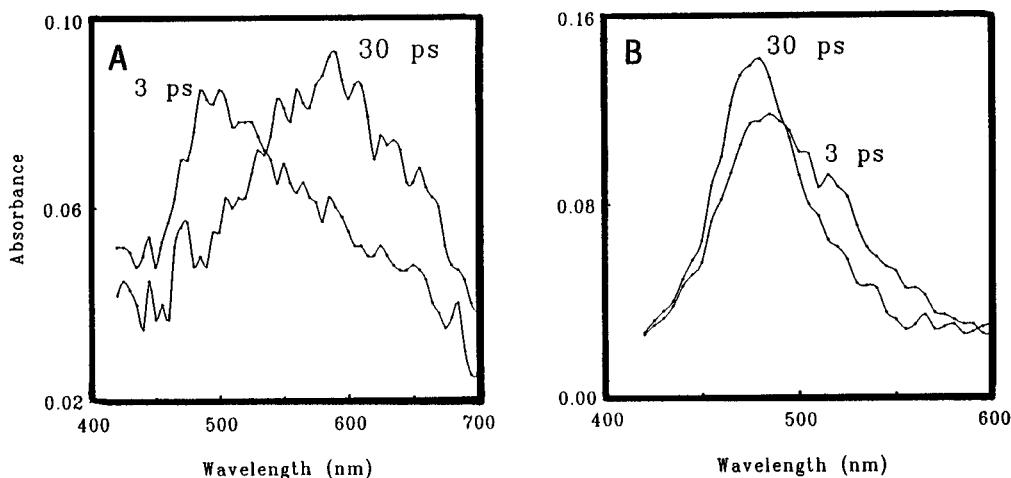
**Figure 9.** Transient spectra recorded at two delay times following the 400-nm excitation of (A) 1,2-naphthoquinone and (B) 9,10-phenanthrenequinone in dichloromethane. The spectra are corrected for chirp.

diffusion-controlled even at 1 M quencher concentration, the first-order rate constant of $k_{obs} = 10^{10}$ s$^{-1}$ observed at this concentration represents the lower limit for the rate of electron transfer from **HEB** to $^3$**CA**\*. Thus despite the substantial difference of 0.6 V between the reduction potentials of $^1$**CA**\* and $^3$**CA**\*,[7,9] electron transfers from **HEB** to singlet and to triplet chloranil are both (indistinguishably) very fast.[45]

The practical use of $^1$**CA**\* as oxidant is hampered by two factors: (i) The short lifetime of the singlet excited state ($\approx 5$ ps) generally excludes diffusional encounter with a donor in solution, and (ii) the rapidity of the (fully spin-allowed) back-electron transfer process ($k_{bet}$ in eq 7) within the singlet radical-ion pair prevents any productive reactions. Nevertheless, we have shown that $^1$**CA**\* is able to react with electron donors prior to intersystem crossing, provided the donor concentration is high enough.[46] Thus, under conditions where the reactive singlet state is already in contact with the quencher as soon as it is formed, electron transfer can compete with intersystem crossing. It is worth emphasizing that the absence of a barrier imposed by diffusion pertains not only to highly concentrated solutions but also to the crystalline solid state, to films and membranes, host−guest assemblies, and, in general, to any restricted or constrained medium.[47] In such environments, the predominant electron-transfer pathways for photoexcited quinones (and other "triplet" sensitizers) may well be exploited on the singlet manifold.

**(b) Intersystem Crossing from Singlet to Triplet Quinones.** The striking result of this study is that chloranil and related quinones exhibit ultrafast intersystem crossing rates ($k_{ISC} \approx 10^{11}$ s$^{-1}$), which are about three orders of magnitude faster than those determined for simple carbonyl compounds such as acetone.[48] Thus, the question arises as to why the ISC rates are ultrafast. In general, rapid intersystem crossing requires both a small energy gap between singlet and triplet states (singlet−triplet splitting) and an efficient spin−orbit coupling (SOC) to facilitate

this spin-forbidden process.[49,50] Spin−orbit coupling, in turn, depends on the electronic configuration (*i.e.* either n,$\pi$\* or $\pi$,$\pi$\*) of the states involved. In particular, SOC is most efficient between a $\pi$,$\pi$\* and a n,$\pi$\* state, but symmetry forbidden between a pair of $\pi$,$\pi$\* or two n,$\pi$\* states.[51]

In the case of chloranil, the energy gap between the S$_1$ and T$_1$ states of about 0.6 eV is sufficiently small to allow rapid intersystem crossing. However, both the lowest excited singlet and the lowest excited triplet state are of n,$\pi$\* character,[52] and thus spin−orbit coupling would be too weak to enhance the direct intersystem crossing from S$_1$ (n,$\pi$\*) to T$_1$ (n,$\pi$\*). To explain the ultrafast ISC rates for chloranil and the other quinones, we suggest that intersystem crossing occurs through an intermediate state with $\pi$,$\pi$\* configuration.[55] Such a putative state has been invoked to explain the ultrafast intersystem crossing of benzophenone (*vide supra*),[50] for which ultrafast intersystem crossing takes place from S$_1$ (n,$\pi$\*) to T$_2$ ($\pi$,$\pi$\*) due to strong spin−orbit coupling. The T$_2$ state is then rapidly deactivated by internal conversion to produce the T$_1$ (n,$\pi$\*) state. For the quinones, spin−orbit coupling between the n,$\pi$\* and $\pi$,$\pi$\* states is indeed optimized, as demonstrated not only by the ultrafast intersystem-crossing rates but also by the lack of heavy-atom effect[56] in the series from fluoranil to iodanil (see Table 2). In other words, the spin−orbit coupling cannot be improved any further by the introduction of heavy-atom substituents, which are known to enhance weak spin−orbit coupling significantly.[57]

The ultrafast ISC rates of chloranil and the related quinones in Table 2 are not significantly different in solvents such as acetonitrile and dichloromethane of widely differing polarity. This lack of solvent dependence can be explained by considering the structures and dipole moments of the excited states. For example, a comparison of the calculated structure of benzo-

(45) Based on the driving forces calculated for both electron-transfer processes, *i.e.*, $\Delta G_o = -0.46$ eV for $^3$**CA**\* and $\Delta G_o = -1.08$ eV for $^1$**CA**\*, the rate constants are near the maximum of the bell-shaped Marcus plot, where $\Delta G_o$ changes do not affect the rate constants significantly. See: Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(46) Similar electron-transfer quenching of an extremely short-lived ($\tau$ < 10 ps) singlet excited state has been observed for benzophenone.[41]

(47) (a) Ramamurthy, V. *Photochemistry in Organized and Constrained Media*; VCH Publishers: New York, 1991. (b) Kalayanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.

(48) (a) An ISC rate constant of $5 \times 10^8$ s$^{-1}$ has been reported for acetone. See Nau, W. M.; Cozens, F. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 2275. (b) For other examples, see: Lee, E. K. C.; Lewis, R. S. *Adv. Photochem.* **1980**, *12*, 1.

(49) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429.

(50) Unett, D. J.; Caldwell, R. A. *Res. Chem. Intermed.* **1995**, *21*, 665.

(51) (a) El-Sayed, M. A. *J. Chem. Phys.* **1962**, *36*, 573. (b) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834.

(52) It is assumed that the energy diagram of chloranil is similar to that of the parent benzoquinone.[53] Moreover, the n, $\pi$\* character of S$_1$ and T$_1$ states has been established for *o*-naphthoquinone[39] and phenanthrenequinone.[54]

(53) Itoh, T. *Chem. Rev.* **1995**, *95*, 2351.

(54) Shimoishi, H.; Tero-Kubota, S.; Akiyama, K.; Ikegami, Y. *J. Phys. Chem.* **1989**, *93*, 5410.

(55) For benzoquinone, a series of higher triplet states of various configurations have been identified spectroscopically. See Itoh in ref 53.

(56) Khudyakov, I. V.; Serebrennikov, Y. A.; Turro, N. J. *Chem. Rev.* **1993**, *93*, 537.

(57) For the heavy-atom effects in substituted naphthalenes as a typical example, see: Ermolaev, V. L.; Svitashev, K. K. *Opt. Spectrosc.* **1965**, *7*, 399.

quinone triplet ($T_1$) with its ground state ($S_0$) shows that, despite a lengthening of the C−O bonds in the triplet state, the $D_{2h}$ symmetry is not affected.[58] Moreover, the absence of solvatochromism in the ground-state spectrum[11] indicates that no significant change in the dipole moment occurs during the transition from the $S_0$ to the $S_1$ state. We thus conclude that the dipole moments of all three states (*i.e.* the ground state and the singlet and triplet excited states) are similar and close to zero.[59] Under these circumstances, the relative energy levels of the $S_1$ and the $T_1$ states are expected to be insensitive to changes in the solvent polarity.[60]

## Summary and Conclusions

Excited singlet states of quinone sensitizers ($^1Q^*$) undergo ultrafast intersystem crossing (ISC) to the triplet states ($T_1$). This transformation is essentially complete within 20 ps of excitation, and the rate constants $k_{ISC}$ in the order of $10^{11}$ s$^{-1}$ are found to be solvent independent for a variety of substituted quinones in Chart 1. The short but definite lifetime of the singlet quinones provides a temporal window in which it can be quenched by electron donors (D) to yield spin-correlated singlet radical-ion pairs, $^1[D^{\bullet+}, Q^{\bullet-}]$. These ion pairs undergo rapid back-electron transfer in less than 10 ps to regenerate the starting materials, as examplified by the rate constants of chloranil, $k_{BET} \approx 2 \times 10^{11}$ s$^{-1}$. The rapid reaction of the singlet ion pairs is to be contrasted with the long lifetime of the corresponding triplet ion pairs, which persist for several nanoseconds. The ultrafast intersystem crossing of the singlet state to the triplet state of quinones, combined with the long lifetime of the triplet ion pairs (generated by ET quenching of the triplet), forms the basis for the extensive use of quinones as triplet sensitizers. However, we have shown that efficient ET quenching of the excited singlet states of quinones can also be achieved, and that the inclusion of reactions on both the triplet and the singlet manifolds provides a more complete picture of photoinduced electron transfer to quinone acceptors.

## Experimental Section

**Materials.** Chloranil (Aldrich) and bromanil (Tokyo Kasei) were recrystallized from benzene, and 2,3-dichloro-5,6-dicyanobenzoquinone (**DDQ**, Aldrich) was recrystallized from chloroform. Fluoranil was prepared by the oxidation of tetrafluorohydroquinone (Aldrich) with ceric ammonium nitrate in acetonitrile[61] and was purified by sublimation. Iodanil was prepared from bromanil by the procedure of Torrey and Hunter[62] and was recrystallized from ethyl acetate. 1,2-Naphthoquinone was received from Lancaster Synthesis and purified by sublimation before use. Phenanthrenequinone (Aldrich) and hexaethylbenzene (Fluka) were purified by recrystallization from ethanol. The solvents dichloromethane, acetonitrile, and benzene were purified by standard laboratory procedures.[63] Methanol (Fischer, spectrophotometric grade) was used as received.

**Instrumentation.** The femtosecond laser system has been described previously.[14] Briefly, a Ti:sapphire oscillator (Photonics Industries) was pumped by an argon-ion laser (Coherent Innova 310), and the self-modelocked output was sequentially amplified by a Ti:sapphire regenerative amplifier and a linear multipass amplifier (Photonics Industries), both of which were pumped by the frequency-doubled output of a Nd:YAG laser (Continuum Surelite-I) at 10 Hz. The amplified laser pulses (230 fs, 10 mJ) were frequency doubled with an LBO crystal and the second-harmonic output (360−460 nm) was used as the excitation source in the pump-probe experiment. The residual fundamental light was focused on a cuvette containing a 1:1 mixture of $D_2O$ and $H_2O$ to generate supercontinuum probe light.[64] A dual diode array (Princeton Instruments) was utilized as the detector, and complete transient spectra in a wavelength range between 350 and 750 nm could be recorded in a single shot. The overall response time of the laser spectrometer was determined to be less than 700 fs.[65] The laser spectrometers for the picosecond and nanosecond time scales have been described previously.[66] UV−vis absorption spectra were recorded on a Hewlett-Packard HP8450-A diode-array spectrophotometer.

In laser experiments, solutions of the quinones (5−10 mM) were irradiated in 5-mm quartz cuvettes. Experiments using argon-saturated and air-saturated solutions gave the same results. Transient absorption spectra were acquired as the average of 100−300 laser shots. The spectra were corrected for group velocity dispersion[17] by the following procedure: The spectra recorded at different delay times were computer analyzed to generate a series of time-dependent kinetic traces for wavelengths spaced 5 nm apart. The initial rise of each trace was analyzed, and the time point at which half of the initial absorption signal was reached was taken as time zero for that particular wavelength. These raw chirp corrections were smoothed by fitting the wavelength-dependent chirp to a second-degree polynomial in $\lambda$. The absorbance along the kinetic trace was determined at the nominal delay times, offset by the chirp correction for each wavelength, and the absorbance values were plotted to yield the spectra in Figures 1, 7, and 9. In all cases, the time-resolved spectra showed distinct changes with isosbestic points. The wavelengths (in nm) of the absorption maxima of the excited singlet states ($S_1$), the triplet state ($T_1$), and of the isosbestic points (I) are listed here for the various quinones in dichloromethane. **CA**: $S_1$ (505, $\epsilon = 6100 \pm 300$ M$^{-1}$ cm$^{-1}$), $T_1$ (510, $\epsilon = 7600 \pm 400$ M$^{-1}$ cm$^{-1}$; 480, sh), I (450, 530). **FA**: $S_1$ (470), $T_1$ (460, 495), I (450, 465, 490, 500). **BA**: $S_1$(500), $T_1$ (515), I (540). **IA**: $S_1$ (520, 540), $T_1$ (540), I (560). **DDQ**: $S_1$ (470), $T_1$ (470, 640). **DQ**: $T_1$ (490). 1,2-Naphthoquinone: $S_1$ (500), $T_1$ (600, br), I (540). 9,10-Phenanthrenequinone: $S_1$ (485), $T_1$ (480), I (490). The extinction coefficient of chloranil triplet ($T_1$) in dichloromethane was determined by the method of transient actinometry, as described by Hurley et al. using a solution of benzophenone in benzene as the actinometer.[67] First-order rate constants were determined from the fitting of the time-dependent absorbance changes to a monoexponential decay. The uncertainties in the rate constants were estimated based on the errors in the least-squares fits.

(58) Ball, J. R.; Thomson, C. *Theor. Chim. Acta* **1988**, *74*, 195.

(59) It is likely that other triplet states including the $T_2$ ($\pi, \pi^*$) state also have zero dipole moments. The conclusion that the structures and dipole moments of the singlet and triplet states of quinones are similar is furthermore supported by the similarity of their absorption spectra (see Figures 1, 7, and 9). Thus, for most quinones, the absorption maxima and extinction coefficients in the singlet and triplet spectra are about the same. The principal difference is that the absorption bands of the triplet states show a fine structure, whereas those of the singlet states exhibit a more or less (smooth) Gaussian shape.

(60) If there is a significant change in dipole moment between the $S_1$ and $T_1$ states, an appreciable effect of the solvent polarity on the ISC rate constants is expected. A typical example is fluorenone, in which $k_{ISC}$ changes over two orders of magnitude as the solvent is changed from acetone to cyclohexane. See ref 49.

(61) Wallenfels, K.; Draber, W. *Chem. Ber.* **1958**, *91*, 2819.

(62) Torrey, H. A.; Hunter, W. H. *J. Am. Chem. Soc.* **1912**, *34*, 702.

(63) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1988.

(64) (a) Alfano, R. R. *The Supercontinuum Laser Source*; Springer-Verlag: New York, 1989. (b) Hubig, S. M.; Rodgers, M. A. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. I, p 315.

(65) The response time of the laser spectrometer system was determined by monitoring the rise of the singlet state of 1,8-diphenyloctatetraene in cyclohexane. See: Goldbeck, R. A.; Twarowski, A. J.; Russell, E. L.; Rice, J. K.; Birge, R. R.; Switkes, E.; Kliger, D. S. *J. Chem. Phys.* **1982**, *77*, 3319.

(66) Bockman, T. M.; Karpinski, Z. J.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1970.

(67) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.